methanol; colorless leaflets, m. p. 65–69°. This hydrocarbon was dehydrogenated with selenium at 300° for sixteen hours without any further purification. 1,2-Cyclopentenophenanthrene crystallized from methanol in colorless prisms, m. p. 133–134°. It showed no fluorescence in alcoholic solution.

Anal. Calcd. for $C_{17}H_{14}$: C, 93.53; H, 6.47. Found: C, 92.98, 93.00; H, 6.38, 6.53.

The picrate crystallized from methanol; orange needles, m. p. 131–132°.

Previous investigators[16] found physical properties as follows:

Reference	1,2-Cyclopentenophenanthrene, m. p., °C.	Picrate, m. p., °C.
a	135–136	133–134
b	134.5–135	134.5–135
c	134–135	133–134

Summary

The preparation of 2-amino- and 2-hydroxy-9,10-dihydrophenanthrene from 2-acetyl-9,10-dihydrophenanthrene is described.

β-[2-(9,10-Dihydrophenanthryl)]-butyric acid and β-[2-(9,10-dihydrophenanthryl)]-propionic acid have been subjected to ring closure. In the first case the ring closure takes place, as far as can be determined, in position 3 only; in the second case the ring closure in position 3 is the main reaction, and ring closure in position 1 occurs to a minor extent only. The course of the reactions has been confirmed through characterization of the tetracyclic hydrocarbons, benzanthracene and the cyclopentenophenanthrenes, respectively, obtained from the primarily-formed cyclic ketones.

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[16] (a) Kon, *J. Chem. Soc.*, 1087 (1933); (b) Cook and Hewett, *ibid.*, 1109 (1933); (c) Ruzicka, Ehmann, Goldberg and Hösli, *Helv. Chim. Acta*, **16**, 835 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Preparation and Some Reactions of 1-Halogenoalkynes[1]

BY P. A. MCCUSKER AND R. R. VOGT

As a preliminary to a study of the reactions of the 1-halogenoalkynes, various methods for the preparation of these compounds were investigated. Satisfactory methods are available for the preparation of the iodo compounds, by the iodination of the sodium alkyl acetylides, as reported by Vaughn and Nieuwland,[2] and by the iodination of the alkynylmagnesium halides, as reported by Grignard and Perrichon.[3]

For the preparation of the 1-bromoalkynes the reaction of cyanogen bromide with the acetylenic Grignard reagent has been used by Grignard, Bellet and Courtot.[4] The method of Strauss[5] gives high yields of phenylbromoacetylene but the reaction is slow in the alkyl series. For the preparation of the 1-chloroalkynes this method has not been satisfactory. The only method available for the systematic preparation of the 1-chloroalkynes has been that of Truchet.[6]

Jositsch[7] has prepared phenylbromoacetylene by bromination of the Grignard derivative at low temperatures but did not state his yields nor extend the method to the alkyl series. Modifications of this method of low temperature halogenation of metal alkyl acetylides have been studied and found to be suitable for the preparation of 1-chloro- and 1-bromoalkynes.[8] When the temperature of the reaction mixture is kept low enough, the free halogen can, in certain instances, be made to replace the metal of the metal alkyl acetylide without appreciable polymerization or addition taking place. The preparation of 1-bromo- and 1-chloroheptyne by such a procedure is described in the experimental part.

A number of other chlorinating agents were tried for the preparation of the 1-chloroalkynes. Tertiary butyl hypochlorite, thionyl chloride, calcium hypochlorite and dichloramine T gave little or no chloroalkyne on reaction with the alkali metal or magnesium derivatives of the alkyl acetylenes.

A study of the reactions of the 1-bromoalkynes has been made by Grignard and Perrichon[3] and Truchet[6] has investigated the 1-chloroalkynes. The strength of the carbon–halogen bond in all these compounds is noteworthy. No reactions of

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[1] Paper No. XXI on the chemistry of the alkyl acetylenes and their addition products; previous paper, THIS JOURNAL, **59**, 855 (1937).

[2] Vaughn and Nieuwland, *ibid.*, **55**, 2150 (1933).

[3] Grignard and Perrichon, *Ann. chim.*, **5**, 5–36 (1926).

[4] Grignard, Bellet and Courtot, *ibid.*, **4**, 30 (1915).

[5] Strauss, Kolleck and Heyn, *Ber.*, **63B**, 1868 (1930).

[6] Truchet, *Ann. Chim.*, **16**, 309 (1931).

[7] Jositsch, *Bull. soc. chim.*, [3] **34**, 184 (1905).

[8] The authors wish to acknowledge the helpful suggestions of Dr. J. W. Kroeger during the course of this work.

the 1-halogenoalkynes have been reported which are strictly analogous to the reactions of the alkyl halides. The somewhat positive character of the halogen in these compounds greatly modifies their reactions. Replacement of the halogen by a positive element takes place quite readily but replacement by negative groups is very difficult if possible at all.

It has been found that 1-chloroheptyne can be made to react with potassium cyanide–methanol–water mixtures to form a cyanovinyl ether of the structure $C_5H_{11}C(OCH_3){=}CHCN$. This would appear to be a replacement of the chlorine by cyanogen which would be a typical alkyl halide reaction. In this case, however, the replacement may be preceded by addition of methanol, although the work of Moureu and Lazennac[9] indicates that the cyanoheptyne which would be formed adds methanol rapidly in the presence of potassium hydroxide. When other inert solvents, such as dioxane, were used no reaction between the 1-chloroheptyne and potassium cyanide could be observed.

The 1-bromo- and 1-iodoheptynes gave no appreciable amounts of the cyanovinyl ether when treated with potassium cyanide–water–methanol mixtures as above. Attempts to cause the reaction of sodium acetate in methanol by a similar process yielded only unchanged chloroacetylene after several hours of heating. Refluxing of the chloroalkyne for several hours with sodium methylate in ether suspension gave no reaction.

The addition of methanol to the 1-alkynes through the action of mercuric oxide–boron fluoride catalyst has been described by Killian, Hennion and Nieuwland.[10] A similar reaction has been found to take place with the 1-chloro- and 1-bromoalkynes. Using a large excess of methanol, 2 moles can be added to give 1-halogeno-2,2-dimethoxyalkanes. The presence of the halogen on the acetylenic carbon which might, in accordance with Markownikoff's rule, be expected to direct the addition of the methanol in the opposite manner, is without effect. The methanol adds to the halogenoalkynes in the same manner as it does to the 1-alkynes.

The position of the methoxy groups on carbon atom 2 of these compounds was indicated by their hydrolysis with 15% aqueous hydrochloric acid to the corresponding ketones. The physical constants of the hydrolytic product of 1-bromo-2,2-dimethoxyheptane agree quite closely with the constants of 1-bromoheptanone-2 reported by Grignard and Perrichon.[3] The 1-chloroheptanone-2, obtained by the hydrolysis of 1-chloro-2,2-dimethoxyheptane checked, in boiling point, the compound prepared by Levene and Walti,[11] who reported only boiling point and analysis. Truchet's[6] constants for this compound could not be checked. The physical constants determined by us for this compound, which are listed in Table 1, lead to good agreement between calculated and observed molecular refraction.

Experimental

Preparation of 1-Bromoheptyne.—In a 1-liter, 3-necked flask 0.5 mole of ethylmagnesium bromide was prepared in 500 ml. of anhydrous ether. To this was added slowly 0.5 mole of heptyne-1. The solution was refluxed from two to three hours until no more ethane was given off. By means of a bath of liquid ammonia the solution was cooled to a temperature of −32°. Liquid bromine was then added slowly through a dropping funnel. The bromine reacted immediately with the Grignard reagent, magnesium bromide being precipitated. When about three-fourths of the theoretical amount of bromine had been added, the mixture suddenly developed a dark yellow color. At this point the addition of the bromine was stopped. As the mixture warmed to room temperature the solid magnesium bromide dissolved and a lower layer of magnesium bromide–etherate separated. The mixture was hydrolyzed with dilute hydrochloric acid, washed with saturated sodium carbonate solution and with water, dried over anhydrous sodium sulfate and fractionated. The yield of 1-bromoheptyne, b. p. 69° at 25 mm., $n^{22}D$ 1.4678, d^{22}_4 1.2120, was 70% on the basis of heptyne added and 85% on the basis of bromine used.

When liquid bromine was added to a suspension of the sodium alkyl acetylide in ether at −32° and the procedure followed as above, no bromoalkyne was formed. A mixture of high boiling bromination compounds was obtained which indicated that no reaction took place until after hydrolysis.

Direct chlorination of heptynylmagnesium bromide at −32° gave as the only isolable product, 1-bromoheptyne in 15–20% yields. The remainder of the material consisted of an inseparable mixture of higher boiling polymeric compounds. Attempts to prepare the 1-chloroalkynes by using the alkynylmagnesium chlorides at −32 and −70° were unsuccessful, inseparable mixtures being obtained.

Direct chlorination of ether suspensions of sodium alkyl acetylides at −32° gave 25–30% yields of 1-chloroalkynes. In addition, there was obtained, as the average of several runs, 16% of higher boiling material and 16% of unchanged acetylene. A representative portion of this high boiling material, b. p. 40–57° at 3 mm., d^{25}_4 0.961: gave on analysis 17.2% chlorine. This indicated that the mixture consisted of polymeric derivatives of alkyl acety-

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(9) Moureu and Lazennac, *Bull. soc. chim.*, [3] **35**, 528 (1906).

(10) Killian, Hennion and Nieuwland, This Journal, **56**, 1384 (1934).

(11) Levene and Walti, *J. Biol. Chem.*, **98**, 735 (1932).

TABLE I

Compound	B. p. °C.	B. p. Mm.	d_4 at °C.		n_{D}	MR_{D} Calcd.	MR_{D} Obsd.
$C_5H_{11}C(OCH_3)=CHCN$	124–131	15	0.9205	25	1.4462	44.7	44.3
$C_5H_{11}C(OCH_3)_2CH_2Br$	88	5	1.1857	26	1.4531	54.8	54.6
$C_5H_{11}C(OCH_3)_2CH_2Cl$	80–82	8	0.9842	25	1.4325	51.9	51.3
$C_5H_{11}COCH_2Cl$	80–82	13	.9896	26	1.4387	39.4	39.2

TABLE II

Compound	Halogen, % Calcd.	Halogen, % Found	Mol. wt. Calcd.	Mol. wt. Found
$C_5H_{11}C(OCH_3)_2CH_2Br$	33.4	33.3	239	254[a]
$C_5H_{11}C(OCH_3)_2CH_2Cl$	18.2	18.0	194	200[b]

[a] By the method of Rast. [b] By the cryoscopic method using benzene.

lene and 1-chloroalkyne. To reduce the amount of polymeric material formed lower temperatures were tried. By working at a temperature of −70°, with a bath of solid carbon dioxide in ether, the yield of 1-chloroalkyne was increased to 50% but 10–15% of higher boiling material was always obtained. Use of the potassium alkyl acetylide in place of the sodium compound gave much better results. By this means the replacement of metal by halogen took place quite readily and smoothly and little or no high boiling material was obtained. Yields of 50% on the basis of alkylacetylene added and 70% on the basis of alkylacetylene recovered were obtained by the following procedure.

Preparation of 1-Chloroheptyne.—In a 1-liter, 3-necked flask, fitted with a mechanical stirrer, was placed 400 ml. of liquid ammonia. To this was added a few crystals of ferric nitrate as a catalyst for the formation of potassium amide. In a separate flask 0.5 mole of potassium was dissolved in 300 ml. of liquid ammonia. The potassium solution was added slowly to the rapidly stirred ammonia in small portions, the reaction being allowed to go to completion before more was added. The potassium amide, so formed, remained for the most part in solution in the liquid ammonia. One-half mole of heptyne-1 was then added slowly through a dropping funnel. The formation of the potassium alkyl acetylide took place smoothly. The mixture was stirred for several hours until the greater part of the ammonia had evaporated. At intervals, 100–200 ml. of anhydrous ether was added and the mixture gently warmed to drive off the ammonia. The volume of ether was then made up to 600–700 ml. and the mixture refluxed until no more ammonia was given off. This usually required from one to two hours. The temperature of the mixture was then lowered to −70° with a bath of solid carbon dioxide in ether. Dried chlorine gas, measured with a flowmeter, was passed into the mixture at the rate of 0.5 mole in forty minutes. The mixture was then allowed to come to room temperature, hydrolyzed with water, washed with sodium carbonate solution and again with water, dried over anhydrous sodium sulfate, and fractionated. The 1-chloroheptyne so obtained, b. p. 65° at 45 mm., d^{24}_4 0.9250, n^{24}_{D} 1.4411, was a clear liquid of mild odor. Thorough stirring of the mixture was necessary to obtain good yields. Slower or more rapid addition of the chlorine resulted in decreased yields.

For purposes of comparison 1-iodoheptyne was prepared by iodination of sodium amyl acetylide in ether suspension at −32°. This modification of the procedure of Vaughn and Nieuwland[2] resulted in somewhat decreased yields.

Preparation of 1-Cyano-2-methoxyheptene-1.—In a 1-liter, 3-necked flask fitted with a mechanical stirrer and reflux condenser were placed 18 g. of potassium cyanide, 70 g. of water, 100 g. of methanol and 15 g. of 1-chloroheptyne. The mixture was stirred and refluxed for seven hours. The organic layer was separated. The aqueous layer was extracted with ether and the ether extract added to the organic layer. On fractionation 8 g. (43% yield) of 1-cyano-2-methoxyheptene-1 was obtained.

The same compound has been reported by Moureu and Lazennac,[9] who prepared it by the action of potassium hydroxide in methanol on 1-cyanoheptyne. The physical constants of this compound are listed in Table I. The wide boiling range of the compound may be due, as suggested by the above workers, to a mixture of geometric isomers.

Preparation of 1-Bromo-2,2-dimethoxyheptane.—To 2.5 g. of mercuric oxide was added 4 g. of ether boron fluoride and 10 g. of methanol. The catalyst, prepared by warming the mixture for several minutes, was cooled and added to 200 ml. of methanol containing 34 g. of 1-bromoheptyne, in a 1-liter, 3-necked flask. A voluminous white precipitate formed at once. The mixture was stirred for two hours and let stand overnight. From 2 to 3 g. of anhydrous potassium carbonate was then added and stirring continued for one hour. The liquid was decanted from residual solid and fractionated. When about one-half of the methanol had been distilled off the liquid separated into layers, the lower layer being practically pure bromoketal. The compound was obtained in 60% yield.

By a similar procedure 1-chloro-2,2-dimethoxyheptane was obtained in 30% yield from the 1-chloroheptyne. In Table I are listed the physical constants of these two new compounds. Analytical data are given in Table II.

The precipitate which was formed during the preparation of the halogeno ketals was probably a mercury addition compound. Truchet[6] and others have described the formation of mercury addition compounds when acid mercuric sulfate or mercuric chloride reacted with the 1-halogenoalkynes. The mercuric salt of methanol–boron fluoride appears to form a similiar type of addition compound. The solid formed immediately on mixing of the reactants, was highly insoluble in the usual solvents and could not be recrystallized. The compound had no definite melting point but began to char above 100°. This addition compound was probably an intermediate in the formation of the halogeno ketals.

Summary

1. New methods for the preparation of 1-bromo- and 1-chloroalkynes by the direct action of the halogens on metal derivatives of the alkylacetylenes at low temperatures have been described.

2. Physical constants for 1-chloro-2,2-dimethoxyheptane; 1-bromo-2,2-dimethoxyheptane and 1-chloroheptanone-2 have been reported.

3. Some new reactions of 1-chloro- and 1-bromoalkynes have been reported.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Preparation of Dialkylacetylenes in Liquid Ammonia[1]

BY EDWARD A. BRIED AND G. F. HENNION

Introduction

While there are a number of methods suitable for the preparation of dialkylacetylenes the most common procedure is to alkylate a metal alkylacetylide.[2–6]

The following series of reactions may be thus employed

(a) $HC\equiv CNa + RX \longrightarrow RC\equiv CH + NaX$
(b) $RC\equiv CH + NaNH_2 \longrightarrow RC\equiv CNa + NH_3$
(c) $RC\equiv CNa + RX \longrightarrow RC\equiv CR + NaX$

These reactions have been carried out, stepwise, in liquid ammonia with satisfactory results.[6] A serious disadvantage of such preparations, however, is the time involved, particularly if the intermediate monoalkylacetylene is isolated and purified.

We have observed that reactions (a), (b) and (c) above may be conducted *simultaneously* in liquid ammonia to give the symmetrical dialkylacetylenes in satisfactory yields.[7] The procedure is simply to mix sodium acetylide, sodamide and an alkyl halide or sulfate in liquid ammonia in the molar ratio of about 1:1:2 with vigorous agitation. The success of this method is undoubtedly due to the difference in solubility between sodium acetylide and sodamide, and to the great reactivity of monoalkylacetylenes toward sodamide. Thus the solubility of sodium acetylide is in favor of reaction (a), and the acidic character of the alkylacetylene formed favors reaction (b), even though the sodamide is quite insoluble. The alkylating agent therefore reacts particularly as in reactions (a) and (c). It is surprising that large amounts of alkyl amines were not formed by interaction of the alkyl halides with sodamide.

The method may be adapted to the preparation of unsymmetrical dialkylacetylenes. It is necessary in this case to conduct the three reactions successively, though in the same solution, but without the isolation of intermediate products.

An attempt was made to compare the effectiveness of various alkylating agents in these reactions. At atmospheric pressure the alkyl bromides were found to be the most suitable. In this manner ethyl chloride gave only a 2% yield of diethylacetylene while much better results were obtained with ethyl sulfate and ethyl bromide. Butyl chloride was employed in one of these experiments under a pressure of 150–190 lb. per sq. in. (10–13 atm.). The yield of dibutylacetylene was 32.2% of the theoretical. Had mechanical stirring been provided the yield undoubtedly would have been appreciably greater. No doubt

TABLE I

PHYSICAL PROPERTIES OF DIALKYLACETYLENES

Acetylene	B. p., °C.	B. p., Mm.	d^{25}	n_{D25}[a]	MR Calcd.	MR Found
Diethyl	50	245	0.7263	1.4112	27.90	28.1
	74.5	600				
	81.5	744				
Dipropyl	85.1	169	.7474	1.4225	37.18	37.5
	116.7	498				
	130	744				
Dibutyl	78.8	25	.7673	1.4311	46.39	46.6
	106.3	80				
	115.9	115				
Diamyl	100	14	.7816	1.4374	55.63	55.7
	110	23				
	115	30				
Ethyl-butyl	86.7	169	.7501	1.4230	37.18	37.4
	118.5	498				
	131.8	737				

[a] The refractive indices of these compounds were observed to increase by about 0.0005 unit for each degree drop in temperature.

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(1) Paper XXII on the chemistry of the alkylacetylenes and their addition compounds; previous paper, THIS JOURNAL, **59**, 1307 (1937).

(2) Bourguel, *Ann. chim.*, [10] **3**, 191 (1925); *Compt. rend.*, **179**, 686 (1924).

(3) Heisig, THIS JOURNAL, **53**, 3245 (1931).

(4) Jacobson and Carothers, *ibid.*, **55**, 1622 (1933).

(5) Heisig and Davis, *ibid.*, **57**, 339 (1935).

(6) Vaughn, Hennion, Vogt and Nieuwland, *J. Org. Chem.*, in press.

(7) The authors are indebted to Paul A. Sartoretto for the suggestion of this general reaction.