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]

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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

$$\begin{array}{ll} \text{(a)} & HC{\equiv}CNa + RX \longrightarrow RC{\equiv}CH + NaX \\ \text{(b)} & RC{\equiv}CH + NaNH_2 \longrightarrow RC{\equiv}CNa + NH_3 \\ \text{(c)} & RC{\equiv}CNa + RX \longrightarrow RC{\equiv}CR + NaX \end{array}$$

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.,				MR	
	°C.	Mm.	d^{25}	n_{D25}[a]	Calcd.	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.

alkyl chlorides should prove highly effective if used under pressure with mechanical stirring.

The dialkylacetylenes prepared were fractionally distilled to constant index of refraction in each instance. The physical constants determined for the pure compounds are indicated in Table I.

Experimental

Reagents.—Sodium acetylide was prepared as previously described.[6] Suspensions of sodamide in liquid ammonia were prepared according to the method of Vaughn, Vogt and Nieuwland.[8] Ethyl, propyl, butyl and amyl bromides were prepared by the methods described in "Organic Syntheses."[9] The ethyl chloride was obtained from the du Pont Company and ethyl sulfate from the Eastman Kodak Company. Butyl chloride, from the Commercial Solvents Corporation, was fractionated carefully before use.

Preparation of Dibutylacetylene.—A three-liter three-necked flask was equipped with a dropping funnel, a mercury-sealed motor-driven stirrer and two liquid ammonia-cooled condensers, one mounted above the other. The lower condenser was bulbed and the upper one of the coil type. A vapor vent was attached to the flask for pressure release when flooding occurred in the condensers. Sodium acetylide (1.2 moles in one liter of liquid ammonia) was prepared[6] in this apparatus and 1.6 moles of sodamide (in 500 ml. of liquid ammonia) was added. Butyl bromide (274 g., 2 moles) was added dropwise during the course of two hours with vigorous stirring. Stirring was continued for three hours and then 500 ml. of water was added slowly. The organic layer was separated and washed as follows: with water, dilute hydrochloric acid, again with water, then with dilute sodium carbonate solution and finally with distilled water. The product was dried over calcium chloride and fractionated through a 50-cm. Vigreux column at 80 mm. The yield of dibutylacetylene, after the first distillation, was 97.7 g. (70.8%). Redistillation gave 94.7 g. (68.6%) of product boiling at 104–106° at 79 mm.

Preparation of other Symmetrical Dialkylacetylenes.—Dipropyl and diamylacetylenes were prepared as described above, except that propyl and amyl bromides, respectively, were employed. The yield of dipropylacetylene was 66.4% of the theoretical, and 30% in the case of diamylacetylene.

Diethylacetylene also was prepared as described above. Ethyl bromide, ethyl chloride and ethyl sulfate were individually employed as alkylating agents. The following yields were obtained: from ethyl bromide, 47%; from ethyl chloride, 2%; from ethyl sulfate, 32%.

Preparation of Ethylbutylacetylene.—Sodium acetylide (1.2 moles in two liters of liquid ammonia) was prepared in the apparatus described above and 137 g. (1.0 mole) of butyl bromide added dropwise with vigorous stirring. After three hours 1.6 moles of sodamide in 0.5 liter of liquid ammonia was added. After stirring for thirty minutes 191 g. (1.75 moles) of ethyl bromide was added dropwise. After again stirring for thirty minutes 500 ml. of water was added. The organic layer was treated as described above. Distillation (at 742 mm.) yielded 70.2 g. (64% yield) of ethylbutylacetylene, b. p. 129–132°.

Preparation of Dibutylacetylene in Autoclave.—Sodium acetylide (3.2 moles in 2 liters of liquid ammonia) was mixed mechanically with 3.6 moles of sodamide separately prepared in 1 liter of liquid ammonia. The mixture was poured into an autoclave which had been precooled by the addition of 1 liter of liquid ammonia. Butyl chloride (555.2 g., 6 moles) was mixed with 1 liter of liquid ammonia and added to the autoclave contents. The autoclave head was fixed in place and the whole allowed to stand for twenty hours. The maximum pressure reading was 190 lb. per sq. in. (13 atm.). The autoclave pressure was released slowly through a needle valve during a period of ten hours. The autoclave was then opened and 60 g. of ammonium chloride in 0.5 liter of liquid ammonia added to destroy the excess sodamide. One liter of water was added slowly and the autoclave contents transferred to a separatory funnel. The organic layer was treated as described before. The yield of dibutylacetylene was 134 g. (32.3% yield). There was recovered 63 g. of butylacetylene and about 16 g. of butyl chloride. The separation of butylacetylene and butyl chloride could not be accomplished conveniently. The yield of dibutylacetylene, corrected for these by-products, was therefore of the order of 40%.

Summary

A convenient method for the preparation of dialkylacetylenes is described. The process involves the interaction of sodium acetylide, sodamide and alkyl halides in liquid ammonia. Intermediate products are not isolated, thereby effecting a substantial saving of time as compared with older methods.

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(8) Vaughn, Vogt and Nieuwland, THIS JOURNAL, **56**, 2120 (1934).

(9) "Organic Syntheses," Coll. Vol., I, John Wiley and Sons, Inc., New York, 1932, p. 26.