

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

Some Reactions of Dialkylacetylenes¹

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Introduction

A previous communication² in this series reported a rapid preparation of dialkylacetylenes involving the simultaneous interaction of sodium acetylide, sodamide and alkyl halides in liquid ammonia. This work has been extended with three objectives in mind: (1) to study the behavior of higher alkyl halides in the dialkylacetylene synthesis; (2) to study reactions of dialkylacetylenes; and (3) to prepare dialkylacetylene derivatives suitable for rapid identification. Definite results have been obtained only with regard to the first two objectives. A number of noncatalytic addition reactions have been investigated, but in no case have solid derivatives been found suitable for ready identification.

The rapid dialkylacetylene synthesis² is limited definitely to the usage of alkyl halides of moderate molecular weight and appreciable solubility in liquid ammonia. Whereas *n*-butyl bromide gave a 70% yield of dibutylacetylene, *n*-amyl bromide gave a 30% yield of diamylacetylene² and *n*-hexyl bromide a 38% yield of dihexylacetylene. *n*-Octyl bromide, when treated with sodium acetylide and sodamide in liquid ammonia at atmospheric pressure, gave a 57% yield of octylacetylene and a 15% yield of dioctylacetylene. At 120 lb. per sq. in. (8 atm.) the yield of dioctylacetylene increased to 27%, while the yield of octylacetylene amounted to 15%. Decyl bromide gave decylacetylene and decylamine.

Oxidation of dibutylacetylene with 68% nitric acid in the presence of mercuric nitrate resulted in good yields of *n*-valeric acid. Dibutylacetylene rapidly absorbed hydrogen quantitatively at 55 lb. per sq. in. (3.7 atm.) in the presence of Raney nickel to give *n*-decane. In this connection it seems the hydrogenation of dialkylacetylenes may well serve as a source of pure long chain paraffin hydrocarbons. Addition of bromine to dibutylacetylene yielded a dibromide boiling over a 20° range and therefore likely a mixture of *cis* and *trans* isomers. Hydration of dibutylacetylene, using the method recently reported,³ gave 5-

decanone in excellent yield. Catalytic addition⁴ of methanol, ethylene glycol and acetic acid to dibutylacetylene proceeded readily.

Addition of thiocyanogen to diphenylacetylene yielded a crystalline addition compound previously reported by Söderbäck.⁵ Treatment of dibutylacetylene under identical conditions failed to give a derivative. Addition of iodine monobromide to dioctylacetylene in ether yielded a brownish-black solid which decomposed upon heating.

Experimental

Reagents.—Octyl alcohol and decyl bromide were kindly supplied for this work by the du Pont Company.

Reaction of Hexyl Bromide with Sodium Acetylide and Sodamide.—Hexyl bromide (124 g., 0.75 mole) was added dropwise to a mixture of 0.69 mole of sodium acetylide and 0.78 mole of sodamide² in three liters of liquid ammonia during the course of forty-five minutes. The mixture was evaporated to dryness. Ether (200 ml.) and one liter of crushed ice were added, the organic layer separated and treated in the usual manner. Fractionation *in vacuo* through a 30-cm. Vigreux column yielded 27.5 g. (38% yield) of dihexylacetylene boiling at 132–134° at 21 mm. Redistillation gave a product with the following physical constants: b. p. 124° (15 mm.), 140° (25 mm.), 144° (30 mm.); *n*_D²⁰ 1.4330; *d*₄²⁰ 0.7991; *MR* (calcd.), 64.85; *MR* (obsd.), 64.5.

Anal. Calcd. for C₁₄H₂₆: C, 86.51; H, 13.49. Found: C, 85.66; H, 13.46.

Reaction of Octyl Bromide with Sodium Acetylide and Sodamide.—The same procedure was employed as described above. The yield of dioctylacetylene was 14.2 g. (15% yield). There was a recovery of 59.5 g. (57% yield) of octylacetylene and 5.6 g. of octyl bromide. The addition of 100 ml. of dry ether, when half of the octyl bromide had been introduced, did not increase the yield of dioctylacetylene. Octylacetylene (61.6 g., 59% yield) and dioctylacetylene (7 g., 7% yield) were recovered. Preparation of dioctylacetylene in the autoclave at 120 lb. per sq. in. (8 atm.), using the general method previously described,² yielded 25 g. (27% yield) of dioctylacetylene and 15 g. (15% yield) of octylacetylene. Distillation gave dioctylacetylene with the following physical constants: b. p. 163–164° (7 mm.); *n*_D²⁰ 1.4488; *d*₄²⁰ 0.8022; *MR* (calcd.), 83.32; *MR* (obsd.), 83.71.

Anal. Calcd. for C₁₈H₃₄: C, 86.31; H, 13.69. Found: C, 85.76; H, 13.15.

Reaction of Decyl Bromide with Sodium Acetylide and Sodamide.—Two experiments were performed, using 27.6

(1) Paper XXVIII on the chemistry of the alkylacetylenes and their addition compounds; previous paper, *THIS JOURNAL*, **60**, 1714 (1938).

(2) Bried and Hennion, *ibid.*, **59**, 1310 (1937).

(3) Thomas, Campbell and Hennion, *ibid.*, **60**, 718 (1938).

(4) Hennion, Nieuwland, *et al.*, *ibid.*, **56**, 1130, 1384, 1802 (1934); **57**, 2006 (1935).

(5) Söderbäck, *Ann.*, **443**, 142 (1925).

g. (0.125 mole) of decyl bromide with 0.075 mole of sodium acetylide and 0.082 mole of sodamide in each case.

An experiment at atmospheric pressure gave 15 g. of a decyl bromide-decylacetylene mixture, b. p. 72° (3 mm.).

An experiment conducted in the autoclave at 120 lb. per sq. in. (8 atm.) gave 12 g. of decylacetylene and 6 g. of decylamine, weighed as the hydrochloride, m. p. 193°, confirming that reported by Komppa.⁶

Oxidation of Dibutylacetylene.—Seventy-nine grams of 68% nitric acid was placed in a 500-ml. three-necked flask equipped with a dropping funnel, mercury-sealed motor-driven stirrer and water condenser. One gram of mercuric nitrate was dissolved in the nitric acid and 34.5 g. (0.25 mole) of dibutylacetylene added dropwise. The reaction was highly exothermic and it was found possible to maintain a temperature of 80° by controlling the rate of addition of the dialkylacetylene. Stirring was continued for one hour. Benzene (100 ml.) was added, the organic layer separated, washed with water, and fractionated through a 50-cm. Vigreux column. The yield of *n*-valeric acid, after the first distillation, was 34.5 g. (68%). Redistillation gave 30 g. (60% yield) of product boiling at 90–91° (19 mm.). The neutralization equivalent was 100 (molecular weight, calcd., 102).

Hydrogenation of Dibutylacetylene.—A catalytic reduction machine similar to the apparatus described by Adams and Voorhees⁸ was used. A solution of dibutylacetylene (24.2 g., 0.175 mole) in 100 ml. of methanol with 3 g. of Raney nickel catalyst, prepared according to the method of Covert and Adkins,⁹ was shaken in an atmosphere of hydrogen for a period of ninety minutes. The pressure rapidly fell from 55 to 20 lb. per sq. in. (3.7 to 1.3 atm.), corresponding to the absorption of approximately 0.4 mole of hydrogen. The product was washed with 100 ml. of water, the organic layer separated and dried over powdered anhydrous potassium carbonate. Fractionation through a 30-cm. column gave 15.3 g. of product boiling at 62–63° (15 mm.). Successive treatments with concentrated sulfuric acid, water, dilute sodium carbonate and finally with distilled water, followed by distillation, yielded *n*-decane, b. p. 66–67° (17 mm.); n^{25}_D 1.4093; d^{25} 0.7269; *MR* (calcd.), 48.39; *MR* (obsd.), 48.4.

Bromination of Dibutylacetylene.—Bromine (40 g., 0.25 mole) was added dropwise at reflux temperature to a solution of 34.5 g. of dibutylacetylene (0.25 mole) in 200 ml. of dry chloroform. After stirring for one hour, the product was washed successively with water, dilute sodium carbonate, finally with distilled water and dried over calcium chloride. Distillation through a 30-cm. Vigreux column gave a product (50.2 g.) boiling at 113–132° (17 mm.). Repeated fractionation *in vacuo* gave two fractions: (a) b. p. 123–124° (17 mm.); n^{25}_D 1.4975; d^{25} 1.3473; *MR* (calcd.), 63.45; *MR* (obsd.), 64.8; (b) b. p. 127–128° (17 mm.); n^{25}_D 1.5005; d^{25} 1.3749; *MR* (calcd.), 63.45; *MR* (obsd.), 63.8.

(6) Komppa, *J. prakt. Chem.*, **135**, 193 (1932).

(7) The authors are indebted to Mr. M. J. O'Connor, who is now studying the hydrogenation of acetylenes in this Laboratory, for the use of the hydrogenation equipment.

(8) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 53.

(9) Covert and Adkins, *This Journal*, **54**, 4116 (1932).

Anal. Calcd. for $C_{10}H_{18}Br_2$: Br, 53.67. Found: for fraction (a), Br, 53.91; for fraction (b), Br, 53.94.

Hydration of Dibutylacetylene.—Using the general procedure previously described,³ dibutylacetylene (69 g., 0.5 mole) was added dropwise to 225 g. of 70% isopropyl alcohol, in the presence of mercury catalyst, at 80°. Distillation through a 30-cm. column gave 62.4 g. (80% yield) of 5-decanone: b. p. 106–108° (27 mm.); n^{25}_D 1.4225; d^{25} 0.8115; *MR* (calcd.), 48.92; *MR* (obsd.), 48.6.

Anal. Calcd. for $C_{10}H_{20}O$: C, 76.84; H, 12.91. Found: C, 76.48; H, 12.77.

It was found impossible to prepare any of the common ketone derivatives from 5-decanone.

Addition of Methanol to Dibutylacetylene.—Dibutylacetylene (34.5 g., 0.25 mole) was added dropwise to 32 g. (1 mole) of anhydrous methanol, containing the usual catalytic mixture of mercuric oxide, boron fluoride, and trichloroacetic acid.⁴ The product was isolated in the usual manner. The 5,5-dimethoxydecane was found to decompose slowly on distillation. After one distillation the following constants were obtained: b. p. 98–99° (10 mm.); n^{25}_D 1.4245; d^{25} 0.8549; *MR* (calcd.), 60.91; *MR* (obsd.), 60.4.

The decomposition of the dimethoxy compound was accelerated by distillation with a trace of *p*-toluenesulfonic acid.¹⁰ In this manner 32 g. of 5,5-dimethoxydecane gave 27 g. of 5-methoxy-5-decene: b. p. 94–95° (20 mm.); n^{25}_D 1.4310; d^{25} 0.8212; *MR* (calcd.), 54.18; *MR* (obsd.), 53.6. Analysis indicated that the product was impure.

Anal. Calcd. for $C_{11}H_{22}O$: C, 77.57; H, 13.03; CH_3O , 18.2. Found: C, 75.0; H, 11.8; CH_3O , 12.0.

Addition of Acetic Acid to Dibutylacetylene.—Using the general procedure and catalyst described above, 69 g. (0.5 mole) of dibutylacetylene was added dropwise to 36 g. (0.6 mole) of glacial acetic acid containing 5 g. of acetic anhydride. The product was extracted with 150 ml. of ether and the extract washed successively with water, dilute sodium carbonate, finally with distilled water and dried over calcium chloride. Fractionation gave 59 g. (60% yield) of 5-acetoxy-5-decene boiling at 95–97° (10 mm.). The following physical constants were obtained: n^{25}_D 1.4320; d^{25} 0.8663; *MR* (calcd.), 58.81; *MR* (obsd.), 59.3.

Anal. Calcd. for $C_{12}H_{22}O_2$: C, 72.66; H, 11.19. Found: C, 72.04; H, 11.08.

This ester was very resistant both to saponification with alcoholic potassium hydroxide and to hydrolysis with dilute sulfuric acid.

Addition of Ethylene Glycol to Dibutylacetylene.—Dibutylacetylene (69 g., 0.5 mole) was added dropwise to 37.2 g. of ethylene glycol (0.6 mole) according to the general method previously described.⁴ The two liquid phases, which originally prevailed, gradually became homogeneous as the reaction progressed. After distillation the fraction boiling at 105–106° (10 mm.) was retained. Redistillation gave 86.5 g. (86% yield) of 2-butyl-2-amylyl-1,3-dioxolane: b. p. 103–105° (10 mm.); n^{25}_D 1.4339; d^{25} 0.8862; *MR* (calcd.), 58.71; *MR* (obsd.), 58.8.

(10) Killian, Hennion and Nieuwland, *ibid.*, **57**, 544 (1935).

Anal. Calcd. for C₁₂H₂₄O₂: C, 71.93; H, 12.08. Found: C, 71.98; H, 12.04.

Hydrolysis with a small quantity of sulfuric acid gave 5-decanone, b. p. 106–107° (27 mm.); *n*_D²⁰ 1.4225.

Reaction of Thiocyanogen and Iodine Monobromide with Dialkylacetylenes.—A benzene solution of thiocyanogen was prepared according to the method of Söderbäck.⁵ To one-half of this solution was added 1.3 g. of diphenylacetylene in 25 ml. of dry benzene, while to the other was added a comparable quantity of dibutylacetylene. The two solutions were placed in the dark for twenty hours. The diphenylacetylene deposited a crystalline product melting at 192–193°, as previously reported by Söderbäck.⁵ Dibutylacetylene failed to give a derivative.

Diocetylacetylene (2 g.) was added to an ether solution of iodine monobromide (4 g.). After twenty-four hours at room temperature a brownish-black solid was obtained which decomposed upon heating.

Acknowledgment.—The authors acknowledge the kind assistance of Messrs. H. I. Lipsie and C. J. Kelley in a number of experiments.

Summary

1. The action of hexyl bromide, octyl bromide and decyl bromide on mixtures of sodium acetylide, and sodamide in liquid ammonia is described.
2. Oxidation, hydrogenation, bromination, hydration and the addition of methanol, acetic acid and glycol to dibutylacetylene are described.
3. No solid addition compound of dialkylacetylenes, suitable for identification purposes, has been found to date.

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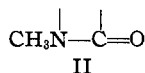
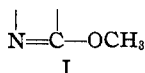
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Pyrimidine Research: The Molecular Rearrangement of 4-Methyl-5-*n*-butyl-2,6-dimethoxypyrimidine¹

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It has long been known that lactim ethers of configuration I will undergo rearrangement to their isomeric and stable lactam form II. These transformations are irreversible and can be brought about by the application of heat with or without the presence of special catalytic agents, and have been observed to take place in both acyclic and cyclic compounds.



This interesting rearrangement recently has been illustrated by Hilbert and Johnson² in the pyrimidine series. They showed that 2,6-dialkoxypyrimidines and 2-oxy-3-alkyl-6-alkoxypyrimidines easily undergo rearrangement on heating without catalytic reagents, at an elevated temperature to form the corresponding 1,3-dialkyl-uracils. Nevertheless, 2,6-dialkoxypyrimidine, containing two lactim configurations within the same pyrimidine molecule, will only undergo partial rearrangement by treatment with methyl iodide at a much lower temperature to form 2-oxy-3-alkyl-6-alkoxypyrimidines.

(1) This paper was constructed from a dissertation presented by C. Wei and N. S. Pan to the Faculty of Chemistry at the University of Kwangsi in partial fulfillment of the requirements for the degree of B. Sci. in June, 1937. The authors especially desire to acknowledge the personal assistance of Professor Treat B. Johnson of Yale University in the preparation of the paper for publication.

(2) Hilbert and Johnson, *THIS JOURNAL*, **52**, 2001 (1930).

In this paper, the authors have extended this study and describe the conditions under which 4-methyl-5-*n*-butyl-2,6-dimethoxypyrimidine III, rearranges to (a) 1,3,4-trimethyl-5-*n*-butyl-uracil IV, and (b) 2-oxy-3,4-dimethyl-5-*n*-butyl-6-methoxypyrimidine V. Thus far, it has been found that the 2,6-dimethoxypyrimidine III easily undergoes transformation into its isomeric and stable lactam configuration, 1,3,4-trimethyl-5-*n*-butyl-uracil IV, by merely heating at 250–270° for three hours. On the other hand, it was only transformed into 2-oxy-3,4-dimethyl-5-*n*-butyl-6-methoxypyrimidine V, under the catalytic influence of methyl iodide at 50 or at 100°. Such partially rearranged pyrimidines like 2-oxy-3,4-dimethyl-5-*n*-butyl-6-methoxypyrimidine V, were only stable, however, at this lower temperature, and undergo further transformation into the isomeric and completely rearranged modification IV by heating. These respective changes are expressed by the formulas.

1,3,4-Trimethyl-5-*n*-butyl-uracil, IV, was identical with the pyrimidine prepared by methylation of 4-methyl-5-*n*-butyluracil. 2-Oxy-3,4-dimethyl-5-*n*-butyl-6-methoxypyrimidine very easily underwent hydrolysis by treatment with dilute hydrochloric acid yielding 3,4-dimethyl-5-*n*-butyl-uracil. The dimethoxypyrimidine III required for this research was synthesized by the action of