[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Preparation and Physical Constants of Acetylenic Compounds

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We have prepared a series of acetylenic derivatives from sodium acetylides in liquid ammonia by methods which are known.[1,2] Modified experimental procedures have supplied in markedly increased yields large quantities of material of good quality, from which samples of high purity have been prepared. Physical measurements have been obtained which are either new, or else more precise than those of the literature.

All syntheses were performed at atmospheric pressure in boiling ammonia. The advantage of these conditions has been stated[1] and partly put to practice before.[3] We have found it convenient to carry out all operations under a Dry Ice reflux condenser built of block tin; this permitted the condensations to reach completion over extended periods of time, at a uniform low temperature, and without losses or unpleasant odors. Lengthened reaction periods and continuous stirring were the main factors improving the yields, while the low temperature prevented side reactions.

The preparation of sodium acetylides from sodium amide is described elsewhere.[4] They were caused to react with organic halides, sulfates and oxygenated compounds. As expected,[1] bromides and sulfates proved the best alkylating agents. It should be remembered that in dialkyl sulfates, only one of the alkyl groups is available. It was found convenient to operate on four-mole quantities, in two liters of ammonia held in a five-liter flask. A Hershberg[5] stirrer provided sufficient stirring. The length of time required to complete the condensation increased with chain length and amount of branching, going from five to twenty-two hours for the bromides used, and giving yields frequently higher than 90%.

Attempts to prepare allyl-acetylenes failed. Both allyl chloride and allyl bromide reacted at once with sodium acetylide, to give up to 93% of an orange unstable derivative, boiling about 145–155° with decomposition, d^{20}_4 0.813, n^{20}_D 1.471. This compound gave a bright yellow cuprous derivative and was probably[6] $HC\equiv CCH(CH=CH_2)CH_2CH=CH_2$ obtained by allylation of $HC\equiv CCHNaCH=CH_2$; it polymerized when hydrogenation was attempted.

Dialkyl acetylenes were prepared in one or in two steps. The one step process consisted in treating disodium acetylene with an alkyl halide; it is best for, but not limited to,[7] symmetrical compounds. The two-step process consisted in first preparing a monoalkylacetylene, then alkylating its sodium derivative. Our yields were about 65% net.

Results in agreement with the literature[1,8] were observed in the action of sodium acetylide on dihalides. Dihalides of the 1,1- and of the 1,2-type failed. $Br(CH_2)_3Br$ reacted vigorously to give a 74% yield of condensed material from which distillation at 120 mm. removed 46% of 1,6-heptadiyne b. p. 60° (120 mm.). In the heads there was a compound amounting to 15%, m. p. −117.6°, b. p. 59.2°, d^{20}_4 0,7415, n^{20}_D 1.4491, which might have been 2-pentene-4-yne. The remainder was tarry material. $Br(CH_2)_3Cl$ reacted with only one mole of sodium acetylide to yield 57% of 5-chloro-1-pentyne, b. p. 67–69° (145 mm.), d^{20}_4 0.968, n^{20}_D 1.445, calcd. Cl, 34.6; found Cl, 34.6%. From $Br(CH_2)_5Br$, an 85% yield of 1,8-nonadiyne was obtained.

Of the disubstituted diynes, only one was prepared. Three moles of 1,6-heptadiyne was added to 7 moles of sodamide, then 7 moles of methyl bromide was slowly allowed to react over a period of four hours. The condensate amounted to a 93% yield, from which fractional distillation at 10 mm. removed 3% of recovered heptadiyne, 76% of the desired 2,7-nonadiyne, and a small fraction regarded as 1,6-octadiyne.

Acetylenic alcohols were prepared by the known methods[9,10,11] but with more modified details to ensure better yields.

Dimethylethynylcarbinol was made from dried acetone added to sodium acetylide, followed by decomposition of the alcoholate *in situ* by means of powdered ammonium chloride. After boiling off most of the ammonia and dissolving in water, continuous ether extraction yielded 75% of the carbinol, and a few per cent. of 2,5-dimethyl-3-hexyne-2,5-diol. Diethylethynylcarbinol was similarly prepared from diethyl ketone, in 90% yield. Propargyl alcohol was made from formaldehyde in only 11% yield, and painstaking improvements gave only 18%, but when this reaction was repeated here by Dr. M. S. Newman, at a temperature of −65°, and with a reaction period of sixteen hours, the yield improved to 30%. For the preparation of 3-butyn-1-ol, a yield of 57% was obtained when a 30% excess of ethylene oxide was used.

Our physical constants are tabulated, with a list of references to the best values of the litera-

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[1] Vaughn, Hennion, Vogt and Nieuwland, *J. Org. Chem.*, **2**, 1 (1937).

[2] Jacobs, in "Organic Reactions," Vol. 3, in press, John Wiley and Sons, Inc., New York, N. Y., 1945; also A. D. Macallum, U. S. Patent 2,125,384.

[3] Slanina, footnote on page 5 of ref. 1

[4] "Inorganic Syntheses," Vol. 2 in press, McGraw-Hill Book Co., Inc., New York, N. Y., 1944.

[5] Hershberg, *Ind. Eng. Chem.*, *Anal. Ed.*, **8**, 313 (1936).

[6] Lespieau and Journaud, *Bull. soc. chim.*, [4] **49**, 423 (1931).

[7] Bried and Hennion, THIS JOURNAL, **59**, 1310 (1937).

[8] Lespieau and Journaud, *Compt. rend.*, **188**, 1410 (1929).

[9] Campbell, Campbell and Eby, THIS JOURNAL, **60**, 2882 (1938)

[10] Hennion and Murray, *ibid.*, **64**, 1220 (1942).

[11] Kreimeier, U. S. Patent 2,106,182, Jan. 25, 1938.

TABLE I

TABLE OF PHYSICAL CONSTANTS

	New data					
	F. range, °C.	F. p., °C.	B. p., (760) °C.	d^{20}_4	$n^{20}D$	Literature refs.
1-Pentyne	0.13	−106.07	40.25	0.6908	1.3852	12, 20
1-Hexyne	.06	−132.09	71.4	.7156	1.3990	13
1-Heptyne	.04	− 80.93	99.78	.7325	1.4088	13
5-Methyl-1-hexyne	.40	−124.6	91.85	.7274	1.4059	14
1-Octyne	.01	− 79.48	126.25	.7460	1.4159	13
2-Butyne	.03	− 32.32	26.99	.6913	1.3921	12, 16, 17
2-Pentyne	.03	−109.33	56.07	.7104	1.4039	18, 19
3-Hexyne	.20	−105.53	81		1.4115	13
2-Octyne	.1	− 61.6	138.00	.7596	1.4278	13
3-Octyne	.2	−103.9	133.14	.7522	1.4250	13
4-Octyne	.11	−102.55	131.57	.7509	1.4248	13
1,6-Heptadiyne	.9	− 84.84	111.5 110.8 (747)	.8051	1.4423	8
1,8-Nonadiyne	.04	− 27.28	161.98	.8158	1.4490	8
2,7-Nonadiyne	.13	+ 4.30	180.0 179.4 (747)	.8332	1.4674	
$HC\equiv C(CH_2)_2CH_2Cl$			67–9/145	.968	1.445	
$HC\equiv CC(CH_3)_2OH$	.09	+ 3.01	104.0 60 (120)	.8614	1.4212	10
$HC\equiv C(C_2H_5)_2OH$	2.1	− 32.2	138	.8719	1.4383	21
$HC\equiv CCH_2OH$	0.12	− 51.80	113.6	.9478	1.4320	10, 22
$HC\equiv CCH_2CH_2OH$	.3	− 63.6	128.9	.9257	1.4409	10, 11

ture.[8–23] The differences are claimed to be in our favor, because we have been able to ascertain the purity of our samples from the shape of the freezing curves and the narrowness of the freezing ranges. We have worked with much larger quantities than our predecessors, and have used the up-to-date equipment for distillation and cryoscopy of a Research Project for the American Petroleum Institute directed here by Dr. C. E. Boord. The only large discrepancies were for the freezing points of 1-pentyne, 2-pentyne, 3-hexyne and 1,8-nonadiyne (−98°, −101°, −101° and −21°, respectively), for the density of propargyl alcohol (0.915) and for the refractive index of 1,6-heptadiyne (1.451). The worst discrepancy concerns propargyl alcohol, for which Hennion[10] gives a density much higher than ours, but in agreement with the older literature, and yet a refractive index which is in the same range as ours. As Lespieau[22] states that a monohydrate freezing about −17° is formed, we ascertained by analysis that our sample was anhydrous (calcd.: C, 64.2; H, 7.02. Found: C, 64.2; H, 7.15). Then we made up a monohydrate sample by mixing 23.656 g. of alcohol with 7.605 g. of water; this sample had d^{20}_4 0.9678, $n^{20}D$ 1.4120 and froze as a mush in the range of −20 to −60° without showing any significant inflection in the freezing curve.

Summary

The condensation of halides, sulfates, ketones, aldehydes, and oxides with sodium derivatives of acetylene and its homologs has been carried out in liquid ammonia refluxing under a condenser cooled with Dry Ice. The condensation products were obtained in much improved yields. All were purified thoroughly, and physical constants more precise than those of the literature have been tabulated.

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(12) Morehouse and Maas, *Can. J. Research*, **11**, 640 (1934).
(13) Campbell and Eby, THIS JOURNAL, **63**, 2683 (1941).
(14) Bovis, *Ann. chim.*, [10] **9**, 461 (1928).
(15) Picon, *Compt. rend.*, **168**, 825, 894 (1919).
(16) Yost, Osborne and Garner, THIS JOURNAL, **63**, 3492 (1941).
(17) Heisig, *ibid.*, **57**, 339 (1935).
(18) Sherrill, *ibid.*, **60**, 2562 (1938).
(19) Van Risseghem, *Compt. rend.*, **158**, 1694 (1914).
(20) Krieger, THIS JOURNAL, **60**, 2118 (1938).
(21) Locquin and Sung, *Bull. soc. chim.*, [4] **35**, 604 (1924).
(22) Lespieau, *ibid.*, [4] **3**, 638 (1908).
(23) Henry, *Ber.*, **5**, 570 (1872).