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

Some Formaldehyde Derivatives of Acetylenic Hydrocarbons[1]

BY G. F. HENNION AND E. P. BELL

Introduction

With the exception of formaldehyde, most aldehydes and ketones react readily with sodium acetylides in liquid ammonia to yield the various alkynyl carbinols.[2] Since the alkylpropargyl alcohols are more difficult to make, especially from paraformaldehyde, we have been interested in synthesizing some of their derivatives by means of metathetic reactions with monomeric methylene compounds. As typical examples of potentially suitable $A-CH_2-B$ reagents we investigated reactions of several chloromethyl esters, chloromethyl ethers, methylene bromide and methylene sulfate with sodium acetylide and acetylenic Grignard reagents under a variety of conditions.

The chloromethyl esters could be used only in inert organic solvents and gave but poor yields of derivatives of the type $R-C\equiv C-CH_2-O-CO-R'$. The highest yield was 20% of butylpropargyl propionate obtained by adding chloromethyl propionate to sodium butylacetylide suspended in toluene. Coating of sodium alkylacetylides with sodium chloride and further condensations of the desired esters likely account for the low yields. No product was obtained when chloromethyl acetate reacted with a suspension of sodium acetylide in either benzene or ether. In this connection it is interesting to note that sodium butylacetylide and the higher homologs may be very finely dispersed through either benzene or toluene by boiling and stirring while the sodium acetylide suspensions remain relatively coarse and granular. Sodium butylacetylide in ether also remains coarse even after considerable boiling.

The reaction of chloromethyl ethers with acetylenic Grignard reagents in ether solution proceeds somewhat better.[3] The highest yield was 42% of butylpropargyl methyl ether from monochlorodimethyl ether and hexynylmagnesium bromide. The ethyl and *n*-propyl ethers which have been made previously[4] by reaction of the Grignard reagent with the formals were also obtained.

As expected, methylene bromide failed to react with both sodium butylacetylide in liquid ammonia and hexynylmagnesium bromide in ether. In the former reaction, however, considerable tarry material was obtained. On the other hand, methylene sulfate reacted very slowly with an ether solution of hexynylmagnesium bromide and gave a very low yield of a hydrocarbon, presumably 5,8-tridecadiyne. The slowness of the reaction may be due to the very limited solubility of methylene sulfate in ether.

The various products are described in Table I.

TABLE I

CONSTANTS, YIELDS AND ANALYTICAL DATA FOR PRODUCTS

Compound	Yield, %	B. p. °C.	B. p. Mm.	$n^{20}D$	d^{20}_4	Mol. wt. Calcd.	Mol. wt. Obs.[a]	MR Calcd.	MR Obs.	% Carbon Calcd.	% Carbon Obs.	% Hydrogen Calcd.	% Hydrogen Obs.
$C_4H_9-C\equiv C-CH_2-O-CO-CH_3$	16	82-83	7	1.4400	0.9437	154	153	43.42	42.99	70.12	69.93	9.09	9.06
$C_5H_{11}-C\equiv C-CH_2-O-CO-CH_3$[b]	10	79-81	6	1.4440	0.9261	168	163	48.04	48.04	71.38	71.29	9.58	9.48
$C_4H_9-C\equiv C-CH_2-O-CO-C_2H_5$	21	70-71	4	1.4432	0.9246	168	170	48.04	48.16	71.38	71.29	9.58	9.66
$C_4H_9-C\equiv C-CH_2-O-CO-C_6H_5$	10	160-162	2	1.5175	1.0238	216	214	62.90	63.17	77.77	77.55	7.40	7.42
$C_4H_9-C\equiv C-CH_2-OCH_3$[c]	42	80-81	29	1.4329	0.8403	126	127	38.79	38.97				
$C_4H_9-C\equiv C-CH_2-OC_2H_5$	27	77-78	20	1.4334	0.8345	140	140	43.41	43.69				
$C_4H_9-C\equiv C-CH_2-OC_3H_7$	34	60-62	6	1.4360	0.8336	154	151	48.03	48.30	77.92	78.02	11.68	11.86
$(C_4H_9-C\equiv C-CH_2-)_2O$	21	140-142	6	1.4660	0.8862	206	207	64.38	64.61	81.55	81.41	10.67	10.72
$(C_4H_9-C\equiv C-)_2CH_2$	13	108-110	8	1.4728	0.8326	176	170	58.24	57.84	88.63	88.60	11.36	11.23

[a] Cryoscopic in benzene. [b] Boiling point only reported by Moureu and Desmots, *Compt. rend.*, **132**, 1224 (1901). [c] On analysis two separate samples exploded and demolished combustion tubes.

Experimental

Reagents.—Chloromethyl esters,[5] *sym*-dichloromethyl ether[6] and methylene sulfate[7] were prepared by procedures

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(1) Paper XLVI on substituted acetylenes and their derivatives; previous paper, THIS JOURNAL, **65**, 965 (1943).

(2) (a) Campbell, Campbell and Eby, *ibid.*, **60**, 2882 (1938); (b) Froning and Hennion, *ibid.*, **62**, 653 (1940); (c) Hennion and Murray, *ibid.*, **64**, 1220 (1942).

(3) (a) Gauthier, *Ann. chim. phys.*, [8] **16**, 334 (1909); (b) Jozitsch and Orelkine, *J. Russ. Phys.-Chem. Soc.*, **42**, 373 (1910); (c) Yvon, *Compt. rend.*, **180**, 748 (1925); (d) Grédy, *Ann. chim.*, [11] **4**, 42 (1935).

(4) Kranzfelder and Vogt, THIS JOURNAL, **60**, 1714 (1938).

(5) Ulich and Adams, *ibid.*, **43**, 660 (1921).

(6) Vorzhtzov and Yurigina, *Obshecki Khim., Khim. Ser.*, **1**, 49 (1931); *C. A.*, **26**, 4521 (1931).

(7) Délépine, *Compt. rend.*, **129**, 831 (1899).

previously described. Butyl- and amylacetylene were obtained in the usual manner.[8]

Reaction of Chloromethyl Acetate with Sodium Butylacetylide.—Twelve grams of sodium (0.5 mole) was converted to the amide in 800 cc. of liquid ammonia[9] contained in a 2-liter three-necked flask provided with condenser, mercury-sealed stirrer and dropping funnel. Butylacetylene, 41 g. (0.5 mole), was added dropwise and the ammonia allowed to evaporate through the (dry) condenser and a soda-lime tower. When nearly dry, 500 cc. of anhydrous benzene was added. Dry nitrogen was passed through the flask with vigorous stirring and refluxing for about six hours. After cooling, 54 g. (0.5 mole) of chloromethyl acetate, diluted with an equal volume of dry benzene, was added dropwise. The mixture was then refluxed with stirring for one and one-half hours, cooled and poured into ice-water. The organic layer was washed until neutral to litmus, dried over magnesium sulfate and fractionally distilled. The ester was put through a Whitmore-Fenske column and then redistilled through a modified Podbielniak column, both under vacuum. The yield was 12.7 g. or 16%. When repeated with bromomethyl acetate in ether the yield dropped to 9.7%.

Saponification equivalent calculated for butylpropargyl acetate, $CH_3COOC_7H_{11}$, 154; obs., 155.9.

Reaction of *sym*-Dichloromethyl Ether with Hexynylmagnesium Bromide.—One mole of magnesium turnings was converted to the Grignard reagent with ethyl bromide in the usual manner. Eighty-two grams of butylacetylene diluted with an equal volume of dry ether was added slowly and the mixture refluxed until the evolution of ethane ceased. About 0.1 g. of cuprous chloride was introduced[10] and 57 g. (0.5 mole) of *sym*-dichloromethyl ether (diluted with ether) added slowly. After heating for one-half hour and standing overnight, the product was hydrolyzed with ice and acetic acid. The dibutylpropargyl ether was purified as described above. The yield was 22.3 g. or 21%.

Reaction of Methylene Sulfate with Hexynylmagnesium Bromide.—Approximately 0.5 mole of butylacetylene Grignard reagent was prepared as noted above. About 0.1 g. of cuprous chloride was added to the mixture and 55 g. (0.5 mole) of methylene sulfate extracted into it. This was achieved by placing the solid sulfate in a Soxhlet type extractor and refluxing the solvent ether through it. Complete extraction took about fifty-six hours and at the end of this time the mixture was decomposed with ice and hydrochloric acid. The layers were separated, the aqueous layer extracted with ether and the extracts combined with the organic layer. This was washed, dried and the ether distilled off. The small amount of residue was fractionated twice through a 50 cc. Claisen flask with small Vigreux column. The yield was 5.9 g. or 13% of 5,8-tridecadiyne.

Summary

Sodium alkylacetylides and the corresponding Grignard reagents have been treated with a number of formaldehyde derivatives to yield various alkylpropargyl compounds. Nine products are described.

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

[9] Vaughn, Vogt and Nieuwland, THIS JOURNAL, **56**, 2120 (1934).

[10] Danehy, Killian and Nieuwland, *ibid.*, **58**, 611 (1936).

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The Alkaline Degradation of Phenyl-β-lactoside, Phenyl-β-cellobioside and Phenyl-D-gluco-β-D-gulo-heptoside

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In an earlier paper[1] it was shown that phenyl-β-D-glucoside and phenyl-β-D-galactoside are degraded readily by the action of hot, aqueous potassium hydroxide to D-glucosan<1,5>β<1,6> and D-galactosan<1,5>β<1,6>, respectively, whereas the corresponding anomeric phenyl-α-hexosides are attacked only very slowly, if at all, under considerably more drastic conditions. It was suggested that the differences in reactivity might be used as a basis for determining the configuration of the glycosidic carbon atom in these compounds, and in the other anomeric glycosides and sugars with which they may be correlated.

Karrer and Smirnoff[2] found that acetobromo-α-D-glucose will add trimethylamine, and that the resulting tetraacetyl-D-glucosido-trimethylammonium bromide is cleaved readily by hot alkali to form D-glucosan<1,5>β<1,6>; the other products are trimethylamine, acetic acid and hydrobromic acid. If the quaternary ammonium halide has the β-configuration, as Micheel[3] has suggested on the basis of its low rotation, the formation of levoglucosan in the two types of degradation may proceed through similar mechanisms.[4]

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[1] Montgomery, Richtmyer and Hudson, THIS JOURNAL, **65**, 3 (1943).

[2] Karrer and Smirnoff, *Helv. Chim. Acta*, **4**, 817 (1921).

[3] Micheel, *Ber.*, **62**, 688 (1929); Micheel and Micheel, *ibid.*, **63**, 386 (1930).

[4] See Micheel and Micheel, *ibid.*, **63**, 2862 (1930); **65**, 258 (1932), for additional information in regard to possible mechanisms.