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

Preparation, Properties and Derivatives of α-Acetylenic Acids[1]

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Introduction

In continuation of the general investigation of substituted acetylenes, a study has now been made of the normal α-acetylenic monobasic acids. While many compounds of this type have long been known, it was desired particularly to devise a convenient preparation and to characterize some of the products and their derivatives. General methods for the preparation of propiolic acid and its homologs consist in carbonation of either sodium acetylide[2–5] (or sodium alkylacetylides) or of the proper acetylenic Grignard reagent.[6,7] In either case alkylpropiolic acids are prepared from the corresponding alkylacetylenes. Need for the latter as starting material has now been obviated since it has been found possible to prepare alkylpropiolic acids by successive reactions of sodium acetylide[8] with alkyl bromide, sodamide and solid carbon dioxide in good over-all yields. The complete synthesis is indicated by the following equations.

$$H—C{\equiv}C—H + Na \longrightarrow Na—C{\equiv}C—H + {}^1/_2H_2 \quad (a)$$

$$Na—C{\equiv}C—H + RBr \longrightarrow R—C{\equiv}C—H + NaBr \quad (b)$$

$$R—C{\equiv}C—H + NaNH_2 \longrightarrow R—C{\equiv}C—Na + NH_3 \quad (c)$$

$$R—C{\equiv}C—Na + (solid)\ CO_2 \longrightarrow R—C{\equiv}C—COONa \quad (d)$$

$$R—C{\equiv}C—COONa + NaHSO_4 \longrightarrow R—C{\equiv}C—COOH + Na_2SO_4 \quad (e)$$

The reactions (a), (b) and (c) are conducted consecutively in the same liquid ammonia solution. Sodamide for (c) is prepared in liquid ammonia[9] and the whole added to the solution from (b). When (c) is completed the ammonia is boiled off and replaced by ether, benzene or toluene. After carbonation aqueous sodium acid sulfate is added to free the desired acid. Since intermediate products are not isolated numerous manipulations and considerable time are saved. Ether and benzene were found to be about equally suitable for the carbonation (d). No untoward experiences resulted when benzene was used, even though the whole suspension usually solidified during carbonation because of the relatively high freezing point of benzene. Yields in toluene were slightly lower than in either of the above instances.

A small amount of dialkylacetylene was obtained as by-product of each synthesis. This may be explained[10] by assuming reaction of unused alkyl bromide from (b) with the sodium alkylacetylide from (c).

Derivatives of the four alkylpropiolic acids studied were obtained readily. Esterification with methanol and sulfuric acid afforded excellent yields of the esters. These have been treated catalytically[11] with methanol and addition at the triple bond observed. While the di-methanol addition products could not be obtained analytically pure, distillation from a trace of *p*-toluenesulfonic acid[12] gave the mono-addition products in satisfactory yield. The acids added bromine from carbon tetrachloride but would not react with dry hydrogen chloride, even when bismuth trichloride was used as a catalyst.[13] This is similar to the experience of Michael and Shadinger[14] with phenylpropiolic acid.

The methyl alkylpropiolates deposited the amides quantitatively upon reaction with anhydrous ammonia in methanol. The esters treated also with phenylhydrazine,[15] by addition at the triple bond and ring closure, to yield the 1-phenyl-3-alkyl-5-pyrazolones.

The various compounds are described in Table I. The experimental part gives the procedures only for the butyl series; the homologs were prepared in an analogous manner.

Experimental

Preparation of Butylpropiolic Acid.—Sodium acetylide (2.2 moles) was prepared[8] in a 3-liter 3-neck flask using 1.5 liters of liquid ammonia. The solution was cooled to −35° by immersing the flask in a methanol-bath cooled with

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(3) Meunier and Desparmet, *ibid.*, [4] **35**, 481 (1924).
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(5) Jackson and Vaughn, U. S. Patent 2,205,885 (1940).
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(7) Oddo, *Gazz. chim. ital.*, **38**, [I] 625 (1908).
(8) Hennion, *Proc. Ind. Acad. Sci.*, **47**, 116 (1938).
(9) Vaughn, Vogt and Nieuwland, THIS JOURNAL, **56**, 2120 (1934).
(10) Bried and Hennion, *ibid.*, **59**, 1310 (1937); **60**, 1717 (1938).
(11) Killian, Hennion and Nieuwland, *ibid.*, **56**, 1384, 1786 (1934); **58**, 80, 892 (1936).
(12) Killian, Hennion and Nieuwland, *ibid.*, **57**, 544 (1935).
(13) Hennion and Welsh, *ibid.*, **62**, 1367 (1940).
(14) Michael and Shadinger, *J. Org. Chem.*, **4**, 135 (1939).
(15) Moureu and Lazennec, *Bull. soc. chim.*, [3] **35**, 843 (1906).

Table I

Analytical and Physical Data

R	M. p., °C.	B. p., °C. at 10 mm.	n^{20}_D	d^{20}	Mol. wt. Calcd.	Mol. wt. Found[a]	MR Calcd.	MR Found	Analyses Calcd.	Analyses Found	Yield, %
			A. Acetylenic Acids, R—C≡C—COOH								
C_2H_5	50.0	100			98.1	100.2					49
n-C_3H_7	24.5–25.0	111			112.1	112.8					42
n-C_4H_9		122	1.4619	0.978	126.2	126.0	34.07	35.48			48
n-C_5H_{11}[e]		133	1.4595	0.961	140.2	139.6	38.68	39.89			40
			B. Methyl Esters, R—C≡C—$COOCH_3$								
C_2H_5		47	1.4376	0.963	112.1	108.5	29.56	30.54			71
n-C_3H_7		65	1.4409	.946			34.18	35.47			91
n-C_4H_9		72	1.4455	.937			38.80	39.87			84
n-C_5H_{11}		94	1.4464	.926			42.21	44.27			93
			C. Methanol Addition Products of Esters. R—C(OCH_3)=CH—$COOCH_3$						% OCH_3		
C_2H_5		59.5	1.4525	1.016	144.2	138.6	37.36	38.32	42.97	40.91	44
n-C_3H_7		76	1.4544	0.990	158.2	153.0	41.98	43.28	39.23	37.73	44
n-C_4H_9		88	1.4558	.975	172.2	167.4	46.60	47.88	36.04	32.93	52
n-C_5H_{11}		100	1.4564	.965	186.2	184.5	51.21	52.51	33.33	31.32	47
			D. Dibromides, R—CBr=CBr—COOH						% Br		
C_2H_5	35.0–38.5	126[b]			257.9	263.1			61.97	62.34	c
n-C_3H_7		125[d]	1.5462	1.831	272.0	276.5	46.51	47.02	58.78	59.13	
n-C_4H_9		142[e]	1.5376	1.735	286.0	287.9	51.13	51.54	55.89	56.34	
n-C_5H_{11}		146[d]	1.5313	1.648	300.0	302.4	55.75	56.34	53.28	53.08	
			E. Amides, R—C≡C—$CONH_2$						% N[f]		
C_2H_5	146–146.5								14.42	14.37	c
n-C_3H_7	81.5–82.0								12.60	12.54	
n-C_4H_9	68.0–69.0								11.18	11.15	
n-C_5H_{11}	89. –90.0								10.06	10.03	
			F. Pyrazolones, R—C=N—N(C_6H_5)—CO—CH_2 (ring closed C to CH_2)						% N[g]		
C_2H_5	100–100.5				188.2	183.8					62
n-C_3H_7	110.5–111				202.2	198.5					65
n-C_4H_9	83.0–83.5				216.3	211.0			12.95	13.18	54
n-C_5H_{11}	95.5–96.0				230.3	227.3					56

[a] Molecular weights of acids and their dibromides were determined by titration; of other products, cryoscopically in benzene. [b] Six mm. pressure; another fraction was isolated in this preparation having the following properties: m. p., 40.2–43.7°; b. p., 118–125.5 °at 6 mm. Found: mol. wt., 264.8; Br, 66.42. [c] Quantitative. [d] Two mm. pressure. [e] Seven mm. pressure. [f] Kjeldahl. [g] Dumas.

solid carbon dioxide. Two moles (274 g.) of n-butyl bromide was added dropwise, vigorous stirring being maintained for an additional three hours. The temperature of the cooling bath was lowered to −45° and 2.2 moles of freshly prepared sodamide[9] in liquid ammonia added very slowly. One-half liter of absolute ether (or benzene, or toluene) was added, a soda-lime drying tube attached to the vent, and the contents allowed to stand overnight. The mixture was heated over a water-bath for three hours while dry nitrogen gas was admitted to aid in the removal of all ammonia. An additional 500 ml. of diluent was added during this period. Then the flask was cooled and 2 moles of solid carbon dioxide added in small pieces at 20°. The bath was cooled to −50° and solid carbon dioxide continually added in small portions to the reaction mixture until a large excess was present. The contents were then allowed to return to room temperature overnight. Acidification was carried out in an ice-bath by adding dropwise 2.4 moles of a saturated solution of sodium acid sulfate to the agitated mixture. The organic layer and solvent extracts were combined and dried over anhydrous sodium sulfate. The solvent was removed by distillation and the acid purified by fractionation *in vacuo* through a helix-packed, jacketed column (1.5 cm. × 35 cm.). The by-product, dibutylacetylene, was obtained in 5% yield.′

Preparation of Methyl Butylpropiolate.—Esterification was carried out in the usual manner by reaction of 0.67 mole (85 g.) of butylpropiolic acid with a solution of 4 g. of concentrated sulfuric acid in 3.35 moles (107.2 g.) of absolute methanol. After separating, washing and drying the crude ester was purified by vacuum distillation.

Addition of Methanol to Methyl Butylpropiolate.—The catalyst was prepared[11] by heating gently a mixture of 2 g. of red mercuric oxide, 2 ml. of ether–boron fluoride, 10 ml. of absolute methanol and 1 g. of trichloroacetic acid in a 500-ml. 3-neck flask. One mole (32 g.) of absolute methanol was added, and a solution of 0.5 mole (70.1 g.) of methyl butylpropiolate in 1 mole (32 g.) of absolute methanol added dropwise. The temperature was maintained at 50°. After two hours the mixture was allowed to cool to room temperature, then 10 g. of moderately powdered anhydrous potassium carbonate was added. The sludge was permitted to settle overnight, the supernatant liquid decanted and the excess methanol removed by distillation. The residue was fractionated under vacuum. If, on repeated fractionation, the product did not distill at constant index of refraction, a few crystals of *p*-toluenesulfonic acid were added to the combined fractions which were distilled once again.[12]

Addition of Bromine to Butylpropiolic Acid.—To 0.1 mole (12.6 g.) of butylpropiolic acid dissolved in an equal volume of anhydrous carbon tetrachloride was added, dropwise and with constant shaking, 0.1 mole (16 g.) of bromine dissolved in an equal volume of anhydrous carbon tetrachloride. The flask was kept cool and a drop of bromine in excess served to indicate the endpoint of the reaction. All volatile matter was drawn off and the residue distilled under vacuum.

Action of Hydrogen Chloride on Butylpropiolic Acid.—No reaction occurred when dry hydrogen chloride was bubbled for four hours through a warm solution of 0.048 mole (6 g.) of butylpropiolic acid in twice its volume of anhydrous benzene. Bismuth trichloride (1 g.) was ineffective as a catalyst.

Preparation of Butylpropiolamide.—To a solution of 10 ml. of liquid ammonia in 10 ml. of absolute methanol was added 0.035 mole (5 g.) of methyl butylpropiolate. After standing overnight the volatile matter was evaporated from the residue which solidified on cooling. The amide was purified by repeated crystallization from 95% ethanol.

Preparation of 1-Phenyl-3-butyl-5-pyrazolone.—To 0.035 mole (5 g.) of methyl butylpropiolate was added 0.026 mole (2.8 g.) of phenylhydrazine. The mixture was heated at 130° for four hours. The product was washed with ether and repeatedly crystallized from aqueous alcohol.

Summary

1. *n*-Alkylpropiolic acids may be obtained in satisfactory yield by the consecutive reaction of sodium acetylide with alkyl bromide, sodamide and solid carbon dioxide.

2. Four acids were made in this manner and five derivatives of each prepared and characterized.

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The Synthesis of 2-Pentadecenoic and 2-Heptadecenoic Acids

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The synthesis and characterization of the higher unsaturated acids is of importance in connection with the chemistry of fats and oils. A number of unsaturated acids, which have been obtained from natural sources, have not been well characterized and relatively few have been synthesized. The present work describes the preparation of 2-pentadecenoic and 2-heptadecenoic acids by the adaptation of methods previously used. The following series of steps will make clear the method of synthesis which was employed.

$$RCH_2COOH \xrightarrow{Br_2} RCHBrCOOH \xrightarrow{KOH}$$

$$RCHOHCOOH \xrightarrow{Pb(OAc)_4} RCHO \xrightarrow[pyridine]{CH_2(COOH)_2} RCH{=}CHCOOH$$

It will be noted that this series of reactions increases the length of the carbon chain by one, and since acids containing an even number of carbon atoms are readily available, the higher α,β-unsaturated acids containing an uneven number of carbon atoms become more accessible.

Measurements of the absorption spectra of 2-pentadecenoic and 2-heptadecenoic acids are indicated in Fig. 1, together with the corresponding data of van der Hulst[2] for 2-octadecenoic

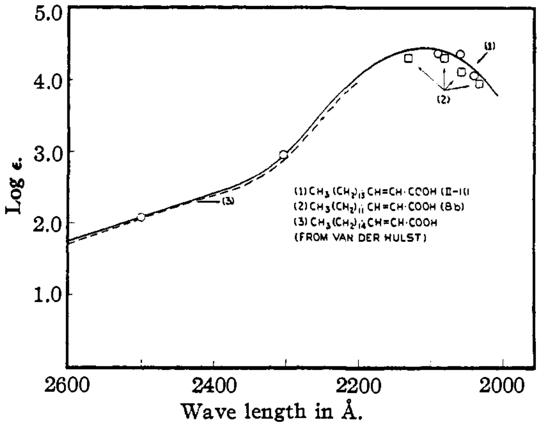

Fig. 1.—Absorption spectra of α,β-unsaturated acids.

acid. The absorption coefficients were determined according to Henri's method described by

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(2) Van der Hulst, *Rec. trav. chim.*, **54**, 639–643 (1935).