N, 8.74; S, 10.00. Found: C, 63.24; H, 7.36; N, 8.89; S, 10.30.

Sulfone of (XVIII).—A sample of the thioether (XVIII) (200 mg.) was oxidized with Superoxol as described for the preparation of the lower homolog. Recrystallization from methanol gave 190 mg. (87% of the theoretical yield) of needles melting at 169–170°.

Anal. Calcd. for $C_{17}H_{24}O_4N_2S$: C, 57.95; H, 6.86; N, 7.94; S, 9.10. Found: C, 57.79; H, 6.59; N, 7.93; S, 9.17.

_dl_-Hexahydro-2-oxo-4-(5-mercaptopentyl)-1-furo-(3,4)-imidazole (XIX).—Five hundred milligrams of the above thioether (XVIII) were cleaved with sodium in absolute ethanol as described for the lower homolog (XV); 250 mg. (70% of the theoretical yield) of the desired material, m. p. 92–94°, was obtained which was purified by recrystallization from ethyl acetate. The substance gave a strong nitroprusside test.

Anal. Calcd. for $C_{10}H_{18}O_2N_2S$: C, 52.15; H, 7.88; N, 12.15; S, 13.90. Found: C, 52.35; H, 7.58; N, 11.82; S, 14.67.

_dl_-Hexahydro-2-oxo-1-furo-(3,4)-imidazole-4-(5-pentane Sulfonic Acid) (IV).—To an ice-cold solution of 200 mg. of the above thiopentanol (XIX) in 10 cc. of water and 1 cc. of acetone, a 0.01 *M* solution of barium permanganate was slowly added with stirring until the solution remained pink for thirty minutes (approximately 76 cc.). The excess of permanganate was destroyed by the addition of 2 cc. of methanol and heating on the steam-bath, and the solution was filtered and concentrated to dryness *in vacuo*. The residue was dissolved in a small amount of water, acetone was added until the solution became cloudy and the barium salt of the sulfonic acid crystallized out. Two hundred fifteen milligrams (71% of the theoretical yield) of the crystalline salt was obtained. The compound was purified by recrystallization from dilute acetone.

Anal. Calcd. for $C_{10}H_{17}O_5N_2SBa/2$: C, 34.70; H, 4.95; N, 8.09; S, 9.27; Ba, 19.86. Found: C, 34.37; H, 5.20; N, 8.14, S, 9.30; Ba, 19.60.

Summary

1. The sulfonic acid analogs of oxybiotin and homoöxybiotin have been prepared.

3. These compounds, as well as several intermediates in their synthesis, were capable of antagonizing the growth-promoting activity of biotin and oxybiotin for several microörganisms.

PITTSBURGH, PA. RECEIVED JULY 15, 1948

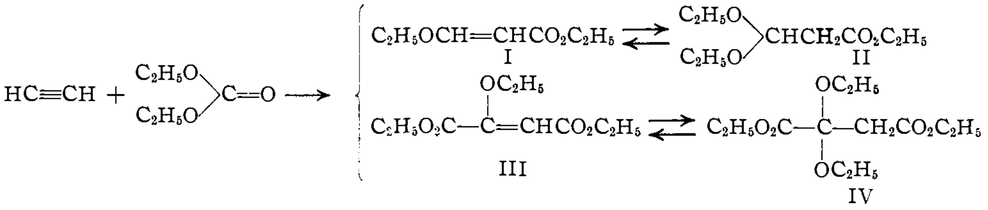
[CONTRIBUTION FROM ROHM & HAAS COMPANY]

Condensation of Acetylenes. Acetylene and Alkyl Carbonates

BY W. J. CROXALL AND H. J. SCHNEIDER

Although alkyl carbonates in the presence of strong bases have been successfully used to introduce the carbalkoxy group into the anions of esters,[1,2,3] ketones[4] and nitriles[5,6] there appears to be no record of the acylation of an acetylene with an alkyl carbonate. This paper describes the results obtained with acetylene and alkyl carbonates.

Preliminary work demonstrated that when ethyl carbonate in the presence of alcohol-free sodium ethoxide was contacted with acetylene at 80° and two to five psi gage pressure, absorption of acetylene occurred over a period of six to eight hours. After neutralization with aqueous acetic acid, distillation of the reaction mixture gave two fractions. The main fraction was a mixture of ethyl β-ethoxyacrylate (I) and ethyl β,β-diethoxypropionate (II). The higher boiling fraction was mostly ethyl α,α-diethoxysuccinate (IV) containing a small amount of ethyl ethoxymaleate (III). The over-all reaction may be represented schematically as follows:



$$HC{\equiv}CH + (C_2H_5O)_2C{=}O \longrightarrow \left\{ \begin{array}{l} \underset{\text{I}}{C_2H_5OCH{=}CHCO_2C_2H_5} \rightleftarrows \underset{\text{II}}{(C_2H_5O)_2CHCH_2CO_2C_2H_5} \\ \underset{\text{III}}{C_2H_5O_2C{-}\overset{OC_2H_5}{\overset{|}{C}}{=}CHCO_2C_2H_5} \rightleftarrows \underset{\text{IV}}{C_2H_5O_2C{-}\underset{OC_2H_5}{\underset{|}{\overset{OC_2H_5}{\overset{|}{C}}}}{-}CH_2CO_2C_2H_5} \end{array} \right.$$

Excess of ester was found to give higher yields of the products and when a twenty to one molar ratio of ethyl carbonate to sodium ethoxide was used, the yields (calculated as mole per cent.) varied between 55–60% based on the ethyl carbonate and acetylene and 175–200% based on the sodium ethoxide. Lower ratios of carbonate to ethoxide gave progressively poorer yields so that when a two to one ratio was used only traces of the products were obtained along with a large amount of non-distillable residue.

Further investigation showed that basic agents other than sodium ethoxide (Method A) were suitable as condensation agents. Sodium acetylide (Method C), disodium acetylide (Method D), and benzyltrimethylammonium ethoxide (Method E) were successfully employed in this reaction with various alkyl carbonates. Table I lists the experiments using these agents with various alkyl carbonates. In all the experiments the yield values

---

[1] Wallingford, Homeyer and Jones, THIS JOURNAL, **63**, 2056 (1941).

[2] Hauser, Abramovitch and Adams, *ibid.*, **64**, 2714 (1942).

[3] Walker, Levine, Kibler and Hauser, *ibid.*, **68**, 672 (1946).

[4] Wallingford, Homeyer and Jones, *ibid.*, **63**, 2252 (1941).

[5] Wallingford, Jones and Homeyer, *ibid.*, **64**, 576 (1942).

[6] Levine and Hauser, *ibid.*, **68**, 760 (1946).

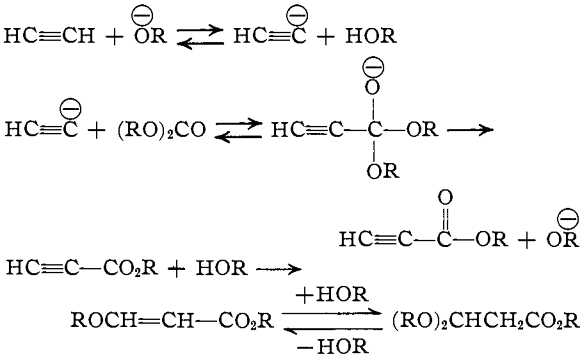
based on the condensation agents were over one hundred per cent. indicating the reaction to be catalytic. Table II lists the physical constants of the products obtained from the various alkyl carbonates.

With sodium alkoxide, a reaction temperature of 80–85° was found to be preferable. Lower temperatures gave slow rates of acetylene absorption, whereas higher temperatures, while increasing the absorption rate, decreased the yields due to non-distillable residues. The initial rate of acetylene absorption with the sodium alkoxides was slow and did not increase appreciably for two to four hours, after which the rate increased and a slightly exothermic reaction occurred over a two-hour period. The rate then became increasingly slow. However, the addition of 0.125 to 0.25 mole of ethyl β-ethoxyacrylate per mole of alkoxide (Method B) to the carbonate, before pressurizing with acetylene, eliminated this induction period so that the absorption of acetylene started immediately. Of all the agents used, sodium alkoxides in general gave the poorest yields.

Mono and disodium acetylide were more active agents than the sodium alkoxides. Reaction with acetylene occurred exothermically at 30–45°, the yields were higher and the amount of the alkyl dialkoxysuccinate fraction was larger than when alkoxides were used. Considerable care was necessary in using these materials with various carbonates; on one occasion when allyl carbonate was mixed with monosodium acetylide, a violent explosion occurred.

Benzyltrimethylammonium methoxide and ethoxide were prepared as alcoholic solutions from benzyltrimethylammonium chloride and the corresponding sodium alkoxide.[7] They were isolated from these solutions by filtration and evaporation under reduced pressure as viscous liquids whose compositions corresponded to equimolecular ratios of quaternary alkoxide to alcohol. Yields were highest with these agents, reaction with acetylene occurring rapidly at room temperature.

The condensation of alkyl carbonates with acetylene is thought to proceed through a series of acid-base type reactions which may be represented by the following ionic mechanisms



$$HC{\equiv}CH + \overset{\ominus}{O}R \rightleftarrows HC{\equiv}\overset{\ominus}{C} + HOR$$

$$HC{\equiv}\overset{\ominus}{C} + (RO)_2CO \rightleftarrows HC{\equiv}C{-}\underset{OR}{\overset{\overset{\ominus}{O}}{C}}{-}OR \longrightarrow HC{\equiv}C{-}\overset{O}{\overset{\|}{C}}{-}OR + \overset{\ominus}{O}R$$

$$HC{\equiv}C{-}CO_2R + HOR \longrightarrow ROCH{=}CH{-}CO_2R \underset{-HOR}{\overset{+HOR}{\rightleftarrows}} (RO)_2CHCH_2CO_2R$$

The first step is the establishment of an equilibrium between acetylene and acetylide ion. It is probable that the equilibrium favors the products on the left-hand side due to (a) the solubility of acetylene in the alkyl carbonate[8] and (b) the stronger acidity of alcohol as compared to acetylene.[9] However, any acetylide ion formed in this equilibrium reacts (see Method C) according to the second step with the alkyl carbonate to give an intermediate ionic complex which releases an alkoxide ion to form an alkyl propiolate. The postulated ionic complex is similar to that advanced by Hauser and Renfrow for the Claisen condensation of esters.[10]

The third step is the addition of alcohol to the alkyl propiolate to give alkyl alkoxyacrylate and alkyl dialkoxypropionate.[11] Although in none of the experiments was it possible to isolate propiolates, their transitory existence seems likely. Their known reactivity with alcohols in the presence of basic catalysts suggests that they immediately react to form the alcohol adducts, namely, the alkoxyacrylate and dialkoxypropionate.[11]

It is therefore evident that in this mechanism the driving force which is capable of shifting the initial equilibrium between acetylene and acetylide ion is represented by the last step in which the alkyl propiolate is converted to the alkyl alkoxyacrylate and the alkyl dialkoxypropionate. The equilibrium existing between acrylate and propionate is undoubtedly in favor of the propionate since only small amounts of acrylate are isolated. That the last step affects the initial equilibrium is partially demonstrated in Method B where alkyl alkoxyacrylate is added to the alkyl carbonate at the beginning of the condensation. In this case, reaction with acetylene starts immediately and no induction period occurs. This procedure presumably removes alcohol in the initial equilibrium to give the alkyl dialkoxypropionate, and allows the formation of acetylide ion.

A possible route for the formation of alkyl alkoxymaleate and alkyl dialkoxysuccinate is indicated in the next formulas.

In this mechanism the alkyl propiolate first undergoes an acid-base exchange and then a series of reactions similar to those outlined for the acrylate and propionate, the intermediate in this case being the alkyl acetylenedicarboxylate. As in the proposed mechanism for the acrylate and propionate, no intermediate acetylenedicarboxylic ester was isolated but only the alcohol addition products of this ester.[11,12]

With disodium acetylide (Method D) it is thought that an initial attack by two molecules of

---

(7) Meisenheimer, *Ann.*, **397**, 295 (1913).

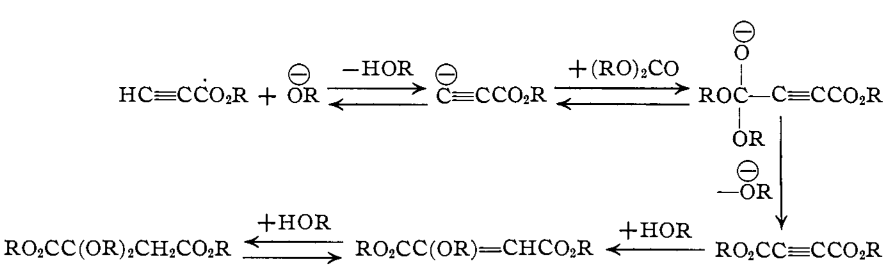
(8) The amount of acetylene required to saturate ethyl carbonate at 40° and five psi gage pressure was found to be 0.5%.

(9) Nieuwland and Vogt, "The Chemistry of Acetylene," Reinhold Publishing Corp., New York City, 1945, state on page 45, . . . the oxyradicals of alcohols and phenols appear to be capable of displacing the ethynyl group. . . .

(10) Hauser and Renfrow, THIS JOURNAL, **59**, 1823 (1937).

(11) Ingold, *J. Chem. Soc.*, **127**, 1203 (1925).

(12) Michael and Bucher, *Ber.*, **29**, 1792 (1896); (see also ref. 11).



alkyl carbonate produces an intermediate doubly charged ionic complex which releases two alkoxide ions to give directly the acetylenedicarboxylic ester. Further condensation with acetylene would then follow the routes indicated above for acrylate-propionate and maleate-succinate formation.

Acknowledgment.—The authors wish to thank Dr. R. Connor for his helpful suggestions and encouragement. The analyses were carried out under the direction of Dr. E. L. Stanley and Mr. C. W. Nash.

Experimental

Materials.—Methyl carbonate was obtained from Pittsburgh Plate Glass Company, Columbia Chemicals Division, and the ethyl carbonate was obtained from U. S. Industrial Chemicals, Inc. Both carbonates were fractionated before use. The higher alkyl carbonates were prepared by alcoholysis of ethyl carbonate with the appropriate alcohol using sodium ethoxide as a catalyst.

Acetylene and Ethyl Carbonate with Sodium Ethoxide.—Method A—The general procedure herein described is representative of all the condensations carried out with acetylene. The others differ only in the type of condensation agent used.

In a 5-liter, 3-necked flask, equipped with a reflux condenser and a gas tight stainless steel stirrer whose blades scraped the bottom of the flask, was placed 800 g. of anhydrous ethanol. While stirring, 57.5 g. (2.5 moles) of clean sodium cut in quarter-inch cubes was added over a period of one hour. The excess ethanol was removed by distillation under vacuum to give white powdered sodium ethoxide. The vacuum was broken by admitting dry nitrogen and 2950 g. (25 moles) of diethyl carbonate was added. In order to remove the last traces of ethanol from the ethoxide–ethyl carbonate mixture, distillation under reduced pressure was continued until a total of 1134 g. of distillate was obtained which consisted of 898 g. of ethyl carbonate and 236 g. of ethanol. Additional ethyl carbonate, 898 g., was then added to the flask so that the final charge was 25 moles of carbonate to 2.5 moles of ethoxide. The flask was then equipped with a thermometer, a gas inlet tube extending below the surface of the liquid and a gas outlet tube which was connected to an open end mercury manometer. With stirring, the mixture was heated to 80°, and acetylene which had been washed with water and concd. sulfuric acid and dried with soda lime was pressed in at five psi gage pressure. The absorption of acetylene was very slow at the start and did not increase appreciably for three hours, at which point the absorption rate began to increase and heating was not necessary. The temperature was held at 80–85° by periodic cooling. A total of 192 g. (7.37 moles) of acetylene was absorbed in seven hours. During the last two hours, the absorption rate was very slow and heating was necessary to maintain the temperature at 80°. The mixture was cooled to room temperature and 653 g. (2.5 moles) of aqueous 23% acetic acid was added. The upper oil layer was separated, the aqueous layer extracted with ether and the extract combined with the oil layer. Distillation through a short packed column, after removal of ether, ethanol and 1620 g. (14 moles) of ethyl carbonate, gave (a) 915 g. of material b. p. 63–65° (2 mm.) and (b) 25 g. of material b. p. 65–110° (2 mm.). There was 223 g. of non-distillable residue.

Fraction (a) had a saponification equivalent of 182. Treatment of a portion of this fraction with a 1% solution of sodium in ethanol gave ethyl β,β-diethoxypropionate, b. p. 65° (2 mm.); $n^{25}\text{D}$ 1.4108[13]; saponification equivalent 192 (calcd. 190).

Anal. Calcd. for $C_9H_{18}O_4$: C, 56.86; H, 9.46. Found: C, 56.90; H, 9.91.

Distillation of a part of fraction (a) from 0.5% of sodium bisulfate gave ethanol and ethyl β-ethoxyacrylate, b. p. 60° (1.8 mm.); $n^{20}\text{D}$ 1.4471; saponification equivalent 145 (calcd. 144).[14]

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.33; H, 8.33. Found: C, 57.96; H, 8.50.

Therefore, from the original saponification equivalent (182), fraction (a) was 87% ethyl β,β-diethoxypropionate and 13% ethyl β-ethoxyacrylate. These percentages check those obtained from a known index of refraction-composition graph. The yield of the propionate–acrylate fraction calculated on a mole per cent. basis was 50.0% on the carbonate consumed, 69.9% on the acetylene and 200% on the sodium ethoxide.

From 600 g. of fraction (b), obtained from a number of runs, there was obtained on fractionation through a two-foot glass helices packed column, 74 g. of ethyl β,β-diethoxypropionate, $n^{20}\text{D}$ 1.4106; 9 g. of an intermediate fraction, b. p. 65° (2 mm.) –85° (0.1 mm.), $n^{20}\text{D}$ 1.4195; 377 g. of ethyl α,α-diethoxysuccinate, b. p. 85° (0.1 mm.), $n^{20}\text{D}$ 1.4305, saponification equivalent 131.5 (calcd. 131) and 106 g. of a higher fraction, b. p. 85° (0.1 mm.) to 98° (0.5 mm.).

Anal. Calcd. for $C_{12}H_{22}O_6$: C, 54.96; H, 8.39. Found: C, 54.95; H, 8.11.

The ethyl α,α-diethoxysuccinate was characterized by hydrolysis with aqueous hydrochloric acid to ethyl oxalacetate according to the method of Michael and Bucher.[12] Treatment of the crude oxalacetate with a copper acetate solution gave the copper salt of ethyl oxalacetate which on recrystallization from anhydrous ethanol formed fine needles, m. p. 156°.[15]

The higher boiling material (106 g.) was refractionated to give 45 g. of ethyl ethoxymaleate, b. p. 97–98° (0.5 mm.); $n^{20}\text{D}$ 1.4562; saponification equivalent 108 (calcd. 108).

Anal. Calcd. for $C_{10}H_{16}O_5$: C, 55.55; H, 7.39. Found: C, 55.59; H, 7.27.

The ethyl ethoxymaleate was characterized by hydrogenation over Raney nickel at 30° and 1500 psi gage pressure to ethyl ethoxysuccinate, b. p. 92–93° (2 mm.); $n^{20}\text{D}$ 1.4217[16]; saponification equivalent 108 (calcd. 109).

Anal. Calcd. for $C_{10}H_{18}O_5$: C, 55.05; H, 8.25. Found: C, 55.01; H, 8.00.

Acetylene and Ethyl Carbonate with Sodium Ethoxide and Ethyl β-Ethoxyacrylate.—Method B—In a similar experiment there was added before the introduction of acetylene, 0.25 mole of ethyl β-ethoxyacrylate. On heating to 80° and pressurizing to five psi gage with acetylene, the absorption of acetylene started immediately, heating was discontinued and periodic cooling was necessary to

---

[13] Dyer and Johnson, THIS JOURNAL, **56**, 222 (1934).

[14] Auwers, *Ber.*, **44**, 3521 (1911).

[15] Wislicenus and Endres, *Ann.*, **321**, 373 (1902), report m. p. 155–156°.

[16] Material prepared according to the method of Purdie, *J. Chem. Soc.*, **39**, 348 (1881), had $n^{20}\text{D}$ 1.4220.

TABLE I

ALKYL CARBONATES AND ACETYLENE

Carbonate	Moles carbonate	Moles condensation agent	Moles acetylene	Method	Yield: Moles: Acrylate	Propionate	Succinate	Moles %[e]: $(RO)_2CO$	C_2H_2
Methyl	25.0	2.5	8.2	A[a]	0.04	1.89	0.93	42.3	35.0
Methyl	15.0	0.5	2.8	C	0.06	0.48	0.94	47.5	52.8
Methyl	5.0	0.25	1.14	D	0.00	0.27	0.49	50.0	66.0
Methyl	6.9	0.23	1.18	E	0.01	0.30	0.58	79.1	75.4
Ethyl	20.0	1.0	2.92	A	0.15	1.42	0.48	53.0	70.5
Ethyl	20.0	1.0	3.20	B	0.13	1.13	0.29	45.0	48.5
Ethyl	10.0	0.5	1.50	C	0.06	0.54	0.46	72.0	71.0
Ethyl	5.0	0.25	1.05	D	0.06	0.52	0.10	97.0	54.2
Ethyl	25.0	0.50	3.69	E	0.23	1.37	1.05	86.0	71.9
n-Butyl	3.0	0.50	1.20	A[b]	0.28	0.29	0.00[d]	33.3	47.5
2-Ethylbutyl	1.5	0.25	0.73	A[c]	0.06	0.43	0.00[d]	81.6	67.5
2-Ethylhexyl	3.0	0.50	0.83	C	0.28	0.44	0.00[d]	29.0	87.5
n-Decyl	2.5	0.50	0.88	A[a]	1.01	0.00	0.00[d]	41.6	>100

[a] $NaOCH_3$ used as catalyst. [b] $NaOC_4H_9$ used as catalyst. [c] $NaOC_8H_{17}$ used as catalyst. [d] Unable to obtain pure by distillation and therefore calculated as loss. [e] The yields are expressed as mole per cent. of the total products based on the reactants consumed.

TABLE II

PHYSICAL CONSTANTS OF COMPOUNDS OBTAINED FROM ALKYL CARBONATES AND ACETYLENE

Compound	B. p. (uncor.) °C.	Mm.	n^{20}_D	d^{20}_{20}	Formula	Analyses, %: Calcd. C	Calcd. H	Found C	Found H	Sapon. equiv. Calcd.	Sapon. equiv. Found
$CH_3OCH{=}CHCO_2CH_3$	56	18	1.4500	1.0801	$C_5H_8O_3$	51.72	6.89	51.19	7.05	116	116
$(CH_3O)_2CHCH_2CO_2CH_3$	77	20	1.4095	1.0445	$C_6H_{12}O_4$	48.65	8.11	48.70	7.88	148	147
$(CH_3O)_2C(CO_2CH_3)CH_2CO_2CH_3$	92	2	1.4335	1.1964	$C_8H_{14}O_6$	46.60	6.80	46.46	7.04	103	103
$(CH_3O)C(CO_2CH_3){=}CHCO_2CH_3$	89–90	0.9	M. p. 40°C.		$C_7H_{10}O_5$	48.28	5.74	48.29	5.68	87	87
n-$C_4H_9OCH{=}CHCO_2C_4H_9$	110	3	1.4505	0.9465	$C_{11}H_{20}O_3$	66.00	10.00	66.12	9.64	200	194
(*n*-$C_4H_9O)_2CHCH_2CO_2C_4H_9$	133	3	1.4278	0.9268	$C_{15}H_{30}O_4$	65.69	10.95	66.04	11.46	274	274
$(C_6H_{13}O)_2CHCH_2CO_2C_6H_{13}$[a]	177–180	3	1.4412	0.9094	$C_{21}H_{42}O_4$	70.39	11.73	70.87	11.83	358	359
$C_8H_{17}OCH{=}CHCO_2C_8H_{17}$[b]	192–203	4	1.4566	0.9080	$C_{19}H_{36}O_3$	73.08	11.54	73.59	12.33	312	312
$(C_8H_{17}O)_2CHCH_2CO_2C_8H_{17}$[b]	195–198	1	1.4470	0.8912	$C_{27}H_{54}O_4$	73.30	12.21	73.20	12.16	442	438
n-$C_{10}H_{21}OCH{=}CHCO_2C_{10}H_{21}$	200	0.1[c]	1.4489	0.8930	$C_{23}H_{44}O_3$	75.00	11.96	74.27	12.46	368	364

[a] 2-Ethylbutyl β,β-di-(2-ethylbutoxy)-propionate. [b] 2-Ethylhexyl β-(2-ethylhexoxy)-acrylate and 2-ethylhexyl β,β-(di-2-ethylhexoxy)-propionate. [c] Falling film still.

maintain the temperature at 80–85°. Over a period of three hours, 4 moles of acetylene was absorbed.

Acetylene and Ethyl Carbonate with Monosodium Acetylide.—Method C—Sodium acetylide (0.54 mole) was prepared in liquid ammonia according to the method of Hennion.[17] The liquid ammonia was allowed to evaporate and the last traces were removed by warming under reduced pressure. Rapidly there was added, with stirring and cooling, 1350 g (15.0 moles) of methyl carbonate.[18] The carbonate–acetylide suspension was warmed to 40° and acetylene was pressed in at five psi gage pressure. The absorption of acetylene started immediately and cooling was necessary to maintain the temperature below 45°. A total of 49 g. (1.93 mole) of acetylene was absorbed in four hours.

Acetylene and Ethyl Carbonate with Disodium Acetylide.—Method D—To 0.25 mole of disodium acetylide[19] there was added cautiously 590 g. (5 moles) of ethyl carbonate.[18] Acetylene was pressed in at five psi gage pressure until a total of 29.5 g. (1.1 mole) of acetylene had been absorbed in two hours. The temperature was maintained at 35–40°.

Acetylene and Ethyl Carbonate with Benzyltrimethylammonium Ethoxide.—Method E—Benzyltrimethylammonium ethoxide was prepared in a manner similar to the method used by Meisenheimer[7] for the preparation of tetramethylammonium ethoxide. From 238 g. (0.43 mole) of a 35.2% ethanolic solution of benzyltrimethylammonium ethoxide there was obtained by evaporation at 40° under reduced pressure (5–1 mm.), 103 g. of the ethoxide containing an equivalent of ethanol. To this was added 1520 g. (12.9 moles) of ethyl carbonate and then 65 g. (2.5 moles) of acetylene over a period of two hours while a temperature of 40–45° was maintained by cooling.

Summary

1. Acetylene condenses with alkyl carbonates in the presence of basic condensation agents to produce alkyl β-alkoxyacrylates, alkyl β,β-dialkoxypropionates, alkyl alkoxymaleates and alkyl α,α-dialkoxysuccinates.

2. A mechanism has been proposed to account for the course of this reaction.

PHILADELPHIA, PA. RECEIVED OCTOBER 19, 1948

---

(17) Hennion, *Proc. Indiana Acad. of Sci.*, **47**, 116 (1938).

(18) Unless sufficient agitation was maintained and adequate cooling provided, violent exothermic reactions occurred at this stage. In one case when dipotassium acetylide was used a violent explosion occurred.

(19) "Inorganic Syntheses," **2**, 80 (1946).