pyrolysis reaction in addition to the four major components of the product mixture. The water was removed prior to analysis with calcium hydride. Trace amounts of a low boiler (degradation product) were formed in negligible quantities and did not alter the product distribution.

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Atmospheric Vinylation of Several Haloacetic Acids and Benzoic Acid by Acetylene

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The vinylation of monochloro-, dichloro-, trichloro-, trifluoroacetic acid and benzoic acid by acetylene at atmospheric pressure in the absence of solvents gave good yields of the vinyl esters. Mercuric oxide, mercuric acetate, and mercuric sulfate were used as catalysts. The infrared and nuclear magnetic spectral data for these compounds have never been reported before in the literature and are now listed for the first time in this report.

The first reported method for the liquid-phase vinylation of organic chloro acids by acetylene was described in a German patent issued in 1912 (*1*). Mono-, di-, and trichloroacetic acids were vinylated by use of acetylene and mercuric salt catalysts. Wiley and Brauer (*17*) reported the preparation of vinyl chloroacetate by a procedure that was an adaptation of that originally employed by Klatte (*9*), Skirrow and Morrison (*15*), and Hermann et al. (*6*). Wiley's preparation was published later (*18*). Unlike the liquid-phase vinylation of acetic acid where zinc and cadmium catalysts are effective, only certain mercuric salts have thus far been found to be effective for chloroacetic acid.

Vinyl chloroacetate was also prepared from acetylene and chloroacetic acid in the vapor phase at 250°C with a zinc-cadmium catalyst (*15*) and in the liquid phase with a mercury catalyst (*6*).

Benzoic acid was vinylated at atmospheric conditions in the gas phase (*3, 5, 7, 10*) and in solution under pressure (*12, 16*). The main catalysts used were zinc or cadmium benzoate on charcoal. The vapor-phase reaction was run at 200–250°C with a 3–5-sec contact time. The solution process was run at 180–185°C (*12*). None of the literature references to date describes a solution process at atmospheric pressure by use of a zinc, cadmium, or mercury catalyst.

The object of this investigation was to explore the feasibility of preparing the vinyl esters (*4, 13, 14*) of several haloacetic acids and benzoic acid with acetylene by using an atmospheric liquid-phase vinylation technique. A further objective was to identify positively the products since few structure proofs and no identifying spectral data are listed in the literature. The detailed investigation of catalysts other than mercury salts will be the subject of a future report.

Experimental

General procedure. To a 250-ml, 3-necked round-bottom flask, fitted with a stirrer, thermometer, gas inlet and outlet tubes, heating mantle, safety flask, flow meter, and Dry-Ice traps for the acetone in the acetylene, were added the appropriate carboxylic acid, mercury catalyst, and approximately 0.20 grams of hydroquinone. The mixture was heated until a solution formed and the mercuric salt was in solution (approx. 20 min.). The acetylene was passed into the hot solution at a given flow rate until at least an amount equivalent to the acid had been added. The acetylene was first passed through a Dry-Ice trap to condense any acetone and then through a safety trap with a mercury valve to indicate atmospheric pressure conditions. The product was either filtered or distilled directly from the reaction flask. Further experimental details are given in Tables I and II. The purity of the products was checked by gas chromatography, ir, nmr, and elemental analyses.

Materials. Mercuric salts and carboxylic acids of the highest grade were obtained from commercial sources and used without further purification.

Analyses. The elemental analyses were performed by Stephen M. Nagy, 78 Oliver Road, Belmont, Mass. The infrared spectra were obtained at the Central Research Laboratory, Chemical Division, Borden, Inc. The nmr data

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were taken near relative to tetramethyl silane on a A-60 A Varian spectrometer by Sadtler Laboratories, Philadelphia, and at Temple University, Philadelphia, Pa.

Results

Table I describes the atmospheric vinylation of several halogenated acetic acids with acetylene at temperatures ranging from 40° to 80°C. Table II describes the atmospheric vinylation of molten benzoic acid with acetylene at temperatures ranging for the most part from 136° to 138°C. Table III describes the infrared and nuclear magnetic spectral properties of the vinyl esters. Table IV describes two kinetic experiments in which the percent vinyl benzoate produced is plotted as a function of time.

Discussion

Halogenated acetic acids. Mono- and dichloroacetic acids were successfully vinylated at atmospheric pressure with mercuric oxide or mercuric sulfate at 60–80°C. Mercuric sulfate (Example 2, Table I) was less effective with monochloroacetic acid when using 0.12 mole catalyst/mole of starting acid (Example 1, Table I). At the same concentration and temperatures, mercuric oxide gave approximately a twofold increase in yield. However, in the case of dichloroacetic acid, both mercury salts were about equally as effective. The use of excess acetylene (Example 3, Table I) did not give any improvement in the vinyl ester yield.

During the course of both reactions the catalyst initially dissolves to some extent, and upon the addition of acetylene a fine gray precipitate forms. Whether the gray precipitate is colloidally dispersed free mercury is not known at this time. At the end of the reaction, free mercury is clearly visible as shiny droplets on the bottom of the flask. The addition of two and three times the normal amount of mercury catalyst during the course of the vinylation reaction did not give improved yields. It appears that the initial catalyst concentration may have formed some coating or deactivating substance so that further additions of catalysts or free acid would be ineffective. Although it was shown by vpc that the starting acid was still present, further vinylation was not possible. The use of zinc and cadmium salts in place of the mercuric oxide or sulfate is presently under investigation.

The reaction of trifluoroacetic acid with acetylene is reported to be effected by using the following catalysts, $HgO/HgSO_4$ (*8*) and HgO/H_2SO_4 (*2*, *11*). The results of Table I indicate that the use of $HgSO_4$ alone with trifluoroacetic acid gives no reaction, but mercuric oxide alone

Table I. Atmospheric Vinylation of Halogenated Acetic Acid with Acetylene

Sample no.	Moles			Temp, °C	Product[a]	Yield, %	Physical constants[a,b,c]	
	RCOOH	CH≡CH	Catalyst				Bp (mm)	nD (°C)
				$CH_2ClCOOH$				
1	2.6	2.6	HgO 0.12 $HgSO_4$ 0.034	60	VCA[d]	48[e]		
2	2.6	2.6	$HgSO_4$ 0.12	56–60	VCA	28[e]		
3	2.6	6.4	HgO 0.06	80	VCA	48[e]	60–64 (39)	1.4450 (24)
4	2.6	5.3	HgO 0.12	80	VCA	67[e]		
5	2.6	1.95	HgO 0.12	60–80	VCA	63[e]		
6	2.6	4.46	HgO 0.12	56–60	VCA	51[e]		
7	2.6	2.6	HgO 0.12	60–80	VCA	78[e]		
8	2.6	2.6	HgO 0.06	60–80	VCA	49[e]		
				$CHCl_2COOH$				
9	1.5	1.5	HgO 0.08	60–80	VDCA[f]	78[e]	35–38 (5–6)	1.4565 (25)
10	1.22	1.22	$HgSO_4$ 0.034	60–80	VDCA	70[e]		
				CCl_3COOH				
11	1.22	3.4	$HgSO_4$ 0.034	60–80	VTCA[g]	68[e]	48–50 (5.0)	1.4657 (23)
12	1.22	1.22	$HgSO_4$ 0.017	60–80	VTCA	3[e]	35–58 (5.0)	
13	1.22	1.22	$HgSO_4$ 0.034	80	VTCA	57[e]	38–40 (4.0)	1.4663 (23)
14	1.22	1.22	HgO 0.046	60–80	NR[h]	...	...	...
15	1.22	1.22	ZnO 0.24	60–80	NR	...	...	...
				CF_3COOH				
16	1.5	1.5	HgO 0.08 $HgSO_4$ 0.034	40–50	VTFA[i]	64[j] 51[e]	44–45	(23)
17	1.5	1.5	$HgSO_4$ 0.034	40–50	NR			
18	1.5	1.5	$HgSO_4$ 0.06	60–65	NR			
19	1.5	1.5	HgO 0.08	40–50	VTFA	61[e]	43–45	1.3150 (23)
20	1.25	1.25	HgO 0.032	40–50	VTFA	47[j] 92[e]		

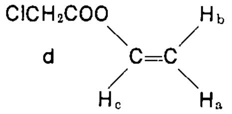
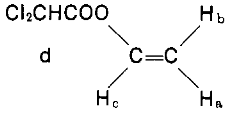
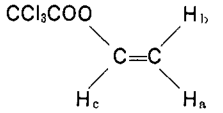
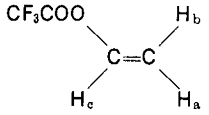
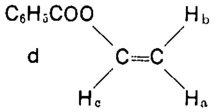
[a] Physical constants obtained in the literature: VCA = $ClCH_2COOCH{=}CH_2$, bp 37–38°C (16.0 mm), $n^{25}D$ 1.4422 (*17*). VTCA = $CCl_3COOCH{=}CH_2$, bp 38–40°C (5.0 mm). The literature is devoid of any index of refraction data (*11*). VTFA = $CF_3COOCH{=}CH_2$, bp 39.5–40.5°C, $n^{25}D$ 1.3151 (*8*). [b] Analysis was unable to be performed by Stephen Nagy. [c] Elemental analyses (C,H,Cl,F) in agreement with theoretical values were obtained and submitted for review. [d] Vinyl chloroacetate. [e] Based on the charged acid. [f] Vinyl dichloroacetate. [g] Vinyl trichloroacetate. [h] No reaction. [i] Vinyl trifluoroacetate. [j] Based on acid used.

Table II. Atmospheric Vinylation of Benzoic Acid with Acetylene to Give Vinyl Benzoate

Sample no.	Moles			Temp, °C	Yield, %	Physical constants[a]	
	Benzoic acid	CH≡CH	Catalyst			Bp (mm)	nD (°C)
1	1.84	7.2	HgO[b] 0.12	136–138	65	52–55 (1–2)	1.5285 (23)
2	2.48	3.6	HgO 0.12	136–138	49		
3	1.84	5.4	HgO 0.12	136–138	46		
4	1.84	2.4	HgO 0.12	136–138	34		
5	1.84	12.6	HgO 0.12	136–138	33		
6	1.84	7.20	HgO 0.12	136–138	33		
7	1.84	7.2	HgO 0.12	136–138	38		
8	1.84	7.2	HgO 0.12	198–200	32		
9	1.84	2.68	HgO 0.12	90–122	51		
10	1.84	9.0	HgO 0.12	136–138	37		
11	1.84	6.5	$Hg(OAc)_2$ 0.12	136–138	58		
12	1.0	1.0	$Hg(OAc)_2$ 0.04	136–138	53		
13	1.0	1.0	$Hg(OAc)_2$ 0.2	136–138	54		
14	1.0	1.0	$Hg(OAc)_2$ 0.01	136–138	52		
15	1.0	1.0	$Hg(OAc)_2$ 0.02	136–138	49		
16	1.0	1.0	$Hg(OAc)_2$ 0.017	136–138	52		
17	1.0	1.0	$Hg(OAc)_2$ 0.014	136–138	25		
18	1.0	1.0	CdO 0.12	136–138	Trace		
19	1.0	1.0	ZnO 0.12	136–138	0		
20	1.0	1.0	BF_3–etherate $Hg(OAc)_2$	136–138	0		

[a] The elemental analyses (C,H) in agreement with theoretical values were obtained and submitted for review. [b] Red or yellow mercuric oxide.

Table III. Spectral Properties of Vinyl Esters

Compound	Ir bands[a]	Nmr data[b]
	3.24 (w), 3.35 (w), 3.40 (s) 5.65 (s), 6.06 (s), 7.08 (m) 7.25 (w), 7.65 (s), 7.81 (s) 8.02 (s), 8.65 (s), 10.37 (m) 10.10 (m), 10.80 (w) 11.37 (m), 12.65 (m)	4.12 s (H_d), 4.55 d 4.65 d (H_a), 4.76 d 5.00 d (H_b), 7.00 d 7.25 d (H_c)
	3.25 (w), 3.35 (w), 5.68 (s) 6.05 (m), 7.10 (w), 7.25 (w) 7.68 (s), 7.80 (s), 7.93 (s) 8.10 (m), 8.30 (m), 8.60 (s) 8.95 (m), 10.15 (m), 10.65 (m) 11.30 (m), 12.27 (s) 12.90 (w), 13.50 (w) 14.85 (w)	4.68 d, 4.78 d (H_a) 4.90 d, 5.12 d (H_b) 6.05 s (H_d), 7.00 d 7.23 d (H_c)
	3.23 (w), 3.35 (w), 5.61 (s) 6.05 (s), 7.71 (s), 8.15 (s) 9.00 (s), 10.05 (s) 10.70 (s), 11.30 (s) 12.15 (s), 13.05 (m), 14.50 (m) 14.95 (s), 15.05 (s)	4.83 d, 4.93 d (H_a) 5.10 d, 5.32 d (H_b) 7.18 d, 7.38 d (H_c)
	3.23 (w), 5.33 (w), 5.57 (s) 6.05 (s), 7.37 (s), 7.53 (m) 8.50 (s) [broad band] 9.57 (m), 10.68 (s) 11.20 (s), 11.65 (s) 12.98 (s), 13.55 (s) 14.50 (w)	5.80 d, 5.90 d (H_a) 5.05 d, 5.25 d (H_b) 7.13 d, 7.33 d (H_c)
	3.25 (w), 3.27 (w), 5.75 (s) 6.06 (s), 6.23 (m), 6.30 (w) 6.70 (w), 6.87 (m), 7.25 (w) 7.65 (m), 7.70 (s), 7.73 (s) 8.00 (s), 8.53 (s), 8.85 (s) 9.17 (s), 9.37 (s), 9.72 (s) 10.57 (m), 11.45 (m), 11.83 (w) 12.50 (w), 14.20 (s), 14.30 (s) 14.85 (w)	4.56 d, 4.66 d (H_a) 4.92 d, 5.15 d (H_b) 4.70 m (H_d) 8.00 d, 8.12 d (H_c)

[a] Recorded neat between NaCl plates. Abbreviations are: (s) strong, (m) medium, (w) weak, (vw) very weak. [b] All chemical shifts are reported in τ values (ppm) relative from tetramethylsilane. Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

Table IV. Percent Vinyl Benzoate Produced During Vinylation of Benzoic Acid with Acetylene at 136–138°C

Sample no.[a] (see Table II)	Time, min	Reaction, %[b]
3	45	29.9
	60	47.2
	90	58.6
	105	61.0
	150	59.8
7	15	2.93
	30	10.2
	45	19.7
	90	47.0
	200	55.4

[a] The composition of 3 and 7 is: 3, benzoic acid 1.84 moles/acetylene 5.40 moles/HgO 0.12 mole; 7, benzoic acid 1.84 moles/acetylene 7.2 moles/HgO 0.12 mole. [b] Calculated by comparing area of vpc peak to that of a standard composition.

gives results equal to the mixture of HgO/$HgSO_4$. Thus, the use of mercuric sulfate offers no particular advantage in this synthesis. A possible reason for the failure of mercuric sulfate in this synthesis and mercuric oxide in the trichloroacetic acid reaction is due to the insoluble nature of these catalysts in their respective systems. Thus, when mercuric sulfate is soluble in trichloroacetic acid, it serves as an efficient catalyst for the vinylation reaction. The data of Table I also indicate that the acetylene route to produce these vinyl esters can be run at relatively low temperature at atmospheric pressure by use of the stoichiometric amount of acetylene. In all cases, the reaction is mildly exothermic during the uptake of the acetylene; this serves as a useful guide as to the extent of the reaction. In all examples cited in Table I, the acetylene was gradually added at approximately 160 ml/min with the aid of a flow meter. In addition, during the course of these reactions, a gray precipitate formed and free mercury was evident in the reaction flask at the end of the reaction. In the examples where no free mercury or gray precipitate formed, there was no evidence of any vinylation reaction.

Since there are few physical constants and no identifying spectral data reported for the vinyl esters—especially the vinyl esters of di-, and trichloroacetic acid—ir and nmr data are listed in Table III. These data are consistent with the structures as being the indicated vinyl esters and thus support the validity of the physical constants listed in Tables I and II.

Benzoic acid. Benzoic acid was vinylated in about 50% yields to vinyl benzoate by use of either mercuric oxide or mercuric acetate. Mercuric oxide was effective at 0.06 mole, and mercuric acetate was effective at only 0.017 mol/mol of benzoic acid. Both catalysts, when used in excess of this amount, gave no improvement in the yield. During the course of the reaction, a gray precipitate formed and at the end of the reaction, free mercury was present as globules on the bottom of the reaction flask.

The use of cadmium oxide and zinc oxide gave poor results in two initial tests, but more experimental work is required before these catalysts are ruled out.

The rate of vinylation of benzoic acid was followed with the aid of vpc, and the peak height of the vinyl benzoate with time was calibrated with standard samples as shown in Table IV. From the data in Table IV, the formation of vinyl benzoate appears to level out at 50–60% conversion. The further addition of fresh catalyst does not change the degree of conversion. This result suggests that some retarding agent is being produced.

Advantage of acetylene over vinyl acetate as a vinylation reagent. The vinyl acetate method fails to vinylate trichloro- and trifluoroacetic acid under a variety of conditions (*13*). Only the acetylene method as described in this report yields the pure vinyl esters. Even dichloroacetic acid yields some by-products when vinylated with the aid of vinyl acetate. Only monochloroacetic acid appears to vinylate favorably with vinyl acetate. However, the latter procedure has the disadvantage that a four to eight molar excess of vinyl acetate is required which considerably adds to the work-up time and final cost of the product. Benzoic acid can be vinylated with either vinyl acetate or acetylene, but the former procedure has similar disadvantages as mentioned above for the vinyl acetate transvinylation of monochloroacetic acid.

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