Table I. Yields and Melting Points of Photoadducts

Maleimide	Adduct yield, %[a]	Adduct mp, °C[b]
2	68	400
3	69 (23)	345
4	76 (30)	392
5	(28)	303–305
6	(34)	340–343
7	20	390

[a] Initial yields after irradiation for 22 hr with a Hanovia 450-W medium-pressure mercury lamp in borosilicate glass test tubes. Numbers in parentheses are yields obtained after irradiating 17 hr with an Ultra-Violet Products PCQ-X1 low-pressure lamp in quartz tubes. [b] All melted with decomposition.

glass test tubes or for 17 hr with an Ultra-Violet Products PCQ-X1 lamp in quartz tubes. The former were irradiated at refluxing benzene temperature; the latter were at about 40°C. No external cooling was employed. Products precipitated on the walls of the test tubes in all cases except with that from maleimide **5** which was remarkably soluble in the reaction medium. The latter was isolated by evaporating the solvent, stirring the residue with boiling ethanol, and filtering off the insoluble adduct. Photoadducts were identical (mp, ir) with bisimides prepared from maleic anhydride–benzene photoadduct (*1, 7*) and the corresponding amines by heating the two together at 200°C until gas evolution ceased (*5*).

Ir: **2** (KBr), 3040, 2920, 1770, 1700, 1590, 1485, 1440, 1370, 1290, 1150, 1105, 1070, 1000, 885, 840, 790, 760, 740, 730, 710, 695, 682, 630 cm^{-1}; **3** (KBr), 2950, 1770, 1700, 1600, 1500, 1475, 1432, 1410, 1365, 1275, 1170, 1110, 1020, 960, 863, 770, 740, 730, 685, 630 cm^{-1}; **4** (KBr), 3100, 2910, 1770, 1700, 1590, 1500, 1370, 1335, 1180, 1155, 1110, 1000, 860, 755, 730, 700, 685, 655 cm^{-1}; **5** (Nujol) 1765, 1700, 1600, 1578, 1490, 1300, 1270, 1190, 1160, 1130, 1085, 1000, 960, 890, 850, 827, 805, 750, 730, 695, 680, 655, 620 cm^{-1}; **6** (Nujol), 1765, 1715, 1600, 1580, 1520, 1348, 1300, 1270, 1243, 1220, 1180, 1150, 860, 848, 790, 783, 755, 724, 705, 690, 650 cm^{-1}.

Irradiation of **3** in benzene in the presence of 0.825*M* trifluoroacetic acid resulted in no photoadduct and quantitative recovery of starting material.

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Synthesis of *cis*- and *trans*-1,2-Dimethoxyethylene by Thermal Demethanolization of 1,1,2-Trimethoxyethane

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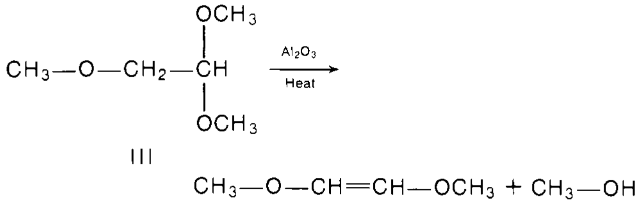
The vapor-phase pyrolysis of 1,1,2-trimethoxyethane over alumina at 300°C is used to produce a cis-rich mixture of *cis*- and *trans*-1,2-dimethoxyethylene in conversions approaching 90%. The cis-trans ratios are typically around eight. The trans-isomer is best prepared by equilibration from the cis-isomer with mercuric acetate catalyst at elevated temperatures (175°C). Some physical properties, including nmr, infrared, and Raman spectra of these isomers, are also reported.

In the course of studying olefin isomerization reactions, we required pure samples of *cis*- and *trans*-1,2-dimethoxyethylene (I and II, respectively). This material was reported in a U.S. Patent (*8*) and by German, Russian, and Japanese workers (*2, 11, 12, 14, 17*). Two main preparative methods were reported: dechlorination of 1,2-dichloro-1,2-dimethoxyethane with Mg (*2, 12, 17*) and pyrolysis of 1,1,2-trimethoxyethane (III) over solid catalysts (*8, 11, 14*). Since we had a supply of III, we decided to use the pyrolytic method originally reported by McElvain and Stammer (*13*) for the preparation of 1,2-diethoxyethylene. It was apparent that we could make substantial improvements in the reported pyrolysis procedures, and we are reporting our results here. In addition, some physical and spectral properties of I and II are also reported.

Results and Discussion

The catalytic decomposition of III proceeds according to the following equation:



$$CH_3{-}O{-}CH_2{-}\underset{OCH_3}{\overset{OCH_3}{CH}} \xrightarrow[\text{Heat}]{Al_2O_3} CH_3{-}O{-}CH{=}CH{-}OCH_3 + CH_3{-}OH$$

III

cis and *trans*
I II

This is entirely analogous to the pyrolysis of 1,1,2-triethoxyethane reported by McElvain and Stammer (*13*).

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A few runs were conducted in batch where III was heated under reflux with base-washed alumina at the boiling point (126°C) under a slow stream of nitrogen. The more volatile products (methanol, I, and II) were entrained by the nitrogen and carried into a cold trap at −40°C. If III were refluxed in the absence of catalyst, no olefins or methanol was produced. Thus, the catalyst Al_2O_3 is essential to the reaction.

In three batch runs lasting up to 80 hr, methanol yield averaged about 80%, but I and II yield varied between 25 and 50%. Thus, as a preparative method, these results are unsatisfactory.

Continuous vapor-phase pyrolysis at higher temperatures appeared to be a more desirable method. The conditions of McElvain and Stammer were tried for the initial pyrolysis runs (*13*). A catalyst bed of base-washed alumina was used rather than Al_2O_3 prepared by hydrolysis of aluminum isopropoxide as employed by the before-mentioned workers. The base-washed material appeared to be entirely satisfactory.

Gresham used silica catalysts impregenated with either barium hydroxide or sodium tetraborate (*8*). His reported pyrolysis temperatures were 50–200° higher than the 300°C we used. Previously (*19*), we had tried ceric oxide on porcelain Raschig rings as pyrolysis catalyst (*1, 3*) at temperatures ranging from 300° to 600°C without success. The pyrolysis apparatus went through many evolutionary changes before the optimum conditions were achieved.

The catalyst could be used repeatedly unless too high reaction temperatures (360°C) were used, in which case, the catalyst appeared dark and burnt. After a successful run, the catalyst was light to medium brown throughout. Initially, the catalyst is white, and for the first hour or so, some decomposition was noticed in the form of a two-phase product mixture. A light yellow-green liquid was obtained initially. When the run was operating successfully (high olefin yields), the product mixture condensed as a light golden liquid. Apparently, the catalyst must be slightly deactivated before high olefin yields are realized (*9, 15, 16*). This type of catalyst deactivation was described for analogous elimination reactions utilizing alumina for the dehydration of alcohols (*7, 10, 18*).

The apparatus shown in Figure 1 was used to produce our optimum runs. In a typical run at 300°C with 296.0 grams (2.467 moles) of III added at the rate of 14.0 g/hr, we obtained the following material balance:

I = 169.8 grams (1.930 moles) 78.3 mol %
II = 20.6 grams (0.234 moles) 9.6 mol %
Methanol = 66.9 grams (2.090 moles) 84.6 mol %
Wt loss = 38.7 grams, 13.1 wt %
I/II = 8.25

The details for the pyrolysis are described in the Experimental section. The weight loss observed presumably was due primarily to the presence of tiny particles which were entrained in the N_2 flow and thus were not condensed.

The continuous pyrolysis was thus an excellent method for preparing the cis-isomer. The trans-material usually represented only $\frac{1}{6}$ to $\frac{1}{8}$ of the cis-compound present in a typical pyrolysis run. The dechlorination of 1,2-dichloro-1,2-dimethoxyethane yields II as the major product (*2, 12, 17*), but this requires further preparation of the dichloro derivative. We can make II by equilibration of I with anhydrous mercuric acetate at elevated temperatures. Thus equilibration of I with 20 wt % of $Hg(OAc)_2$ at 175°C in a glass-lined bomb reactor for 38 hr produced a mixture containing 25.2% of II. After flashing off from the catalyst under vacuum, the II could be separated by careful distillation on a 40–50 plate column.

We report some additional physical and spectral data, most of which has not been reported before, in Table I. The nmr spectra of I and II suggest higher cis-isomer stability if an analogy is made to the case of *cis*- and *trans*-1,2-difluoroethylenes (*4, 6*) in which it is known that the cis-isomer has the lower energy (*5*). The cis-

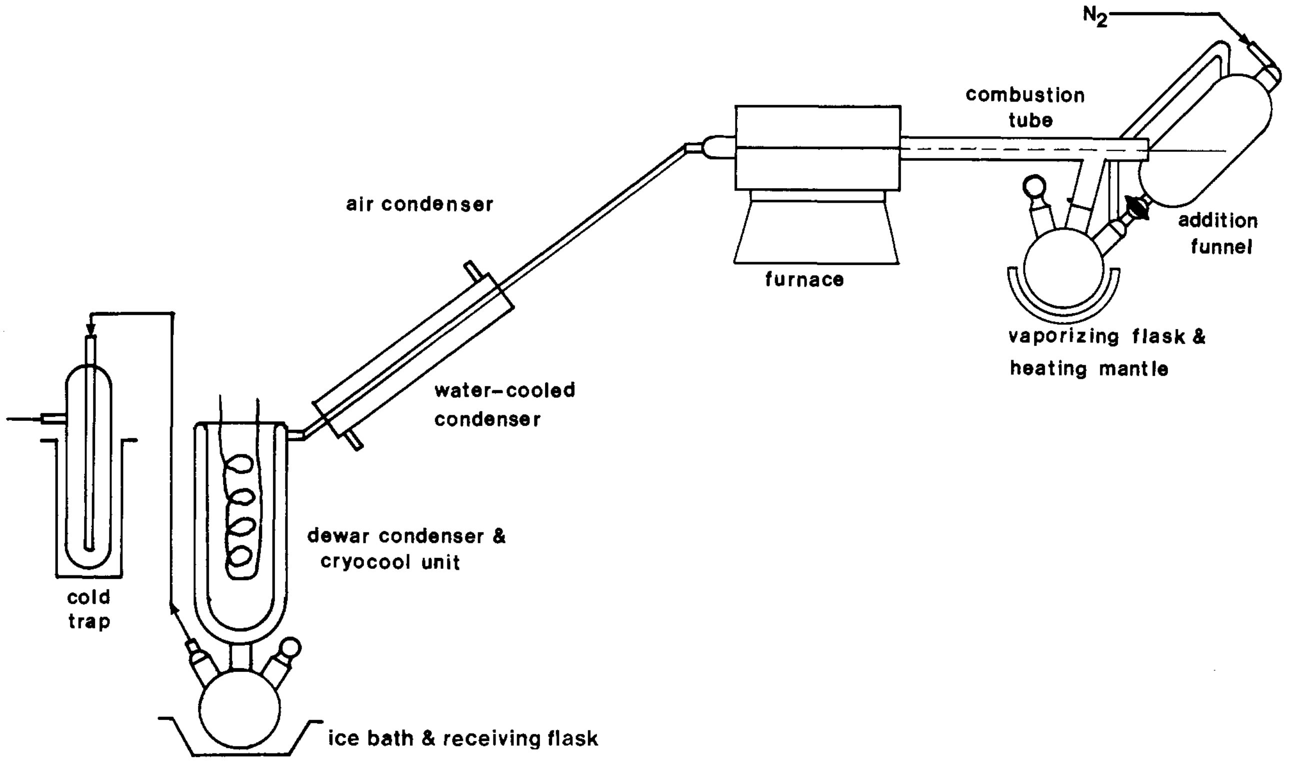

Figure 1. Pyrolysis apparatus

Table I. Physical Properties and Nmr Absorption for *cis*- and *trans*-1,2-Dimethoxyethylene

	cis	trans
Bp	101°C	94°C
ρ, 25°C	0.946 g/ml	0.951 g/ml
$\eta^{29}D$	1.4115	1.4000
M_R,[a] obsd	23.23	22.54
M_R, calcd	23.49	23.49
τ-Methyl protons[b]	6.48	6.60
τ-Vinyl protons[b]	4.88	3.85

[a] M_R was calculated from $\eta^{29}D$ by correcting to 25°C with $\Delta\eta = -0.0004$/degree. [b] Nmr spectra obtained in CCl_4 solution.

Table II. Vibrational Frequencies for *cis*-1,2-Dimethoxyethylene[a]

Raman, cm^{-1}, liquid	Infrared, cm^{-1} Liquid	CCl_4	Gas	Assignment
	3105 (sh)	3105 (sh)		
3065 (m)	3060 (m)	3065 (m)	3065 (m)	ethylenic C—H stretch
3015 (m)	3015 (m)	3020 (s)	3020 (s)	
			2965 (vs)	
2960 (vs)	2955 (vs)	2955 (vs)	2955 (sh)	methyl C—H stretch
2910 (m)	2920 (m)	2920 (s)	2932 (sh)	
2860 (vs)	2850 (vs)	2860 (vs)	2865 (s)	
2815 (m)	2820 (m)	2825 (m)	2835 (m)	
		2730 (w)	2740 (w)	
		2650 (w)		
	2595 (w)	2595 (w)	2605 (w)	
	2500 (w)	2500 (w)		
		2430 (sh)		
	2395 (w)	2400 (w)		
	2360 (vw)	2360 (w)		
	2315 (vw)	2320 (w)		
	2280 (vw)	2285 (vw)	2290 (vw)	
	2250 (vw)	2190 (w)	2200 (vw)	
	2130 (w)	2130 (w)	2145 (w)	
		2110 (sh)		
	2015 (w)	2030 (w)	2045 (w)	
	1935 (vw)			
1825 (vw)	1843 (vw)	1850 (vw)	1870 (vw, b)	
			1768 (vw)	
			1758 (vw)	
		1735 (w)		
1720 (s)	1700 (m)	1702 (m)	1715 (w)	C=C stretch
1690 (vs)	1690 (sh)	1680 (sh)	1690 (sh)	C=C stretch
	1675 (m)	1672 (m)	1680 (m)	
	1655 (sh)	1655 (sh)	1655 (sh)	
		1648 (sh)		
		1638 (sh)		
	1562 (w, b)		1590 (vw, b)	
			1495 (w)	
			1475 (sh)	
1470 (w)	1460 (s)	1462 (sh)	1465 (m)	
1455 (w)		1455 (m)		
		1440 (sh)		
1385 (vw)			1388 (s)	
	1377 (vs)	1375 (vs)	1378 (s)	
1300 (m)	1305 (sh)	1310 (m)	1310 (m)	
	1292 (m)	1288 (m)		
1220 (vw)	1220 (vs)	1218 (s)	1220 (vs)	C—O stretch
1195 (vw)	1188 (sh)	1190 (sh)		
1165 (vw)		1168 (w)		
1120 (vw)	1115 (vs)	1120 (vs)	1133 (vs)	C—O stretch
		1095 (sh)	1105 (sh)	C—O (ir only) stretch
1030 (vw)	1028 (m)	1028 (w)	1033 (w)	
			991 (w)	
980 (vw)	978 (w)	978 (w)	980 (w)	
925 (s)			925 (w)	C—O (Raman only) stretch
	911 (m)	913 (m)	913 (w)	
			889 (w)	
885 (w)	878 (w)	878 (w)	881 (w)	
860 (w)		855 (vw)		
		840 (vw)		
790 (vw)			785 (w)	
745 (w)			740 (m)	
	725 (m)		731 (m)	
		665 (sh)		
	615 (s)	615 (w)	615 (w)	
550 (w)				
380 (s)				

[a] s, strong; m, medium; w, weak; sh, shoulder; v, very; b, broad.

vinyl protons for both cases absorb at approximately 1 ppm higher field than the corresponding trans-isomers. This infers that the cis-double bond is more effectively shielded.

The infrared and Raman spectra of I and II are reported in Tables II and III along with tentative assignments for the bond-stretching frequencies.

Experimental

Batch reactor synthesis of cis- and trans-1,2-dimethoxyethylene, (I and II, respectively). In a 100-ml, three-necked round bottom flask were placed 64 grams (0.524 g-mol) of methoxyacetal (III) and 25 grams (0.245 g-mol) of alumina. The alumina was basic washed and had a 50–200-mesh distribution. The flask was fitted with a reflux condenser, stirrer, thermometer, and nitrogen inlet tube. The reflux condenser was followed by a cold trap (250 × 41 mm), drying tube, and nitrogen bubbler. The cold trap was maintained at −40°C. A slow stream of nitrogen was used to effect a partial take-off procedure. The reaction products and unreacted starting material were collected in the cold trap after 12 hr. The temperature of the refluxing reaction medium was 126°C. Another two runs were carried out with 64.0 and 159.3 grams of III for about 80 hr each. The condensates were combined and distilled to yield 15 grams of I. Recovery of III was 74.0 grams.

Continuous pyrolysis of 1,1,2-trimethoxyethane (III). In the optimum pyrolyses the apparatus shown in Figure 1 was employed. The pyrolysis tube was 1-in. o.d. by 2-ft long and was fitted with a ₮ 24/40 female joint at the inlet end. Fresh alumina (Alcoa grade, regular 8–14 mesh) weighing 75.0 grams was charged into the pyrolysis tube which also contained a 3-ft by $^3/_{16}$-in. pyrex tube with one end sealed. The latter tube served as a receptacle for a thermocouple probe to monitor temperature inside the catalyst bed. Two condensers were placed in series at the exit of the pyrolysis tube. The first was an air condenser (30 × 2 cm) filled with porcelain Raschig rings for heat transfer from the hot vapors. The second (30 × 2 cm) was water cooled and led into the Dewar condenser containing isopropanol in the cold finger and a Cryocool to keep the condenser surface at about −50°C.

Table III. Vibrational Frequencies for *trans*-1,2-Dimethoxyethylene[a]

Raman, cm^{-1}, liquid	Infrared, cm^{-1}			Assignment
	Liquid	CCl_4	Gas	
	3120 (sh)	3120 (sh)	3120 (sh)	
3105 (m)	3105 (sh)	3100 (sh)	3100 (w)	ethylenic C—H stretch
3080 (w)	3085 (m)	3085 (w)	3090 (w)	
3050 (w)	3055 (m)	3050 (w)	3055 (m)	methyl C—H stretch
3015 (m)	3020 (m)	3015 (m)	3020 (s)	
2945 (m)	2960 (s)	2950 (m)	2960 (s)	
2915 (sh)	2925 (s)	2915 (m)	2930 (s)	
			2855 (m)	
2845 (vs)	2850 (s)	2845 (m)	2845 (m)	methyl C—H stretch
	2805 (sh)			
	2600 (vw)		2600 (vw)	
	2430 (vw)	2430 (vw)	2445 (vw)	
	2370 (vw)	2360 (vw)		
	2325 (vw)	2325 (vw)		
	2240 (vw)		2260 (vw)	
	2145 (w)	2150 (vw)	2170 (w)	
	2110 (vw)	2110 (vw)	2130 (w)	
	2070 (vw)	2070 (vw)	2090 (w)	
	1980 (vw)	1985 (vw)	1995 (vw)	
	1935 (vw)			
	1855 (vw)	1850 (vw)		
	1822 (vw)	1825 (vw)		
	1770 (sh)			
	1737 (w)	1737 (vw)		
1688 (m)			1690 (sh)	C=C stretch
1675 (s)			1678 (w)	C=C stretch
1655 (sh)	1670 (m)	1668 (w)	1670 (w)	C=C stretch
		1655 (vw)	1655 (sh)	
			1475 (sh)	
1460 (w)	1467 (m)	1463 (m)	1465 (m)	
	1455 (m)	1452 (m)		
			1385 (w)	
	1375 (w)	1372 (w)	1375 (w)	
1330 (w)	1333 (vw)	1330 (vw)		
1310 (m)	1310 (m)	1310 (w)	1310 (sh)	
	1300 (sh)	1300 (sh)	1298 (m)	
	1292 (m)	1290 (w)	1288 (m)	
1215 (vw)	1218 (vs)	1218 (vs)	1225 (vs)	C—O stretch
			1182 (s)	
			1178 (s)	
1170 (vw)	1172 (vs)	1172 (vs)	1172 (s)	
1155 (vw)				
1125 (vw)	1135 (vs)	1137 (vs)	1145 (vs)	C—O stretch
			1100 (sh)	
1025 (vw)	1020 (sh)	1020 (sh)	1005 (sh)	
995 (w)	995 (m)	995 (m)	992 (m)	C—O stretch
			968 (m)	
	957 (s)	957 (m)	958 (m)	C—O stretch
945 (w)	945 (m)	945 (m)		
			901 (m)	
910 (vw)	900 (s)	897 (m)	892 (m)	
785 (w)	785 (w)		782 (w)	
	735 (vw)	730 (w)	730 (w)	
		672 (vw)	670 (vw)	
		665 (vw)		
635 (vw)				
605 (vw)	605 (w)	605 (w)		
475 (vw)				
365 (vw)				
320 (vw)				
290 (vw)				
225 (vw)				
190 (vw)				

[a] s, strong; m, medium; w, weak; sh, shoulder; v, very.

The condenser led into a three-necked receiving flask. A cold trap, nitrogen bubbler, and drying tube completed the train. Figure 1 shows the entire apparatus.

A slow steady stream of nitrogen was maintained 3–4 hr before the refrigeration apparatus was turned on in the Dewar condenser. This prevented moisture and ice from forming inside the condenser walls and contaminating the reaction product mixture. Similarly, the oven furnace was turned on during this "warm-up" phase. This is an important point since the presence of water caused a two-phase azeotrope (bp 84°C) to form upon fractionation of the final product mixture.

At an average rate of 2 ml/min 296.0 grams of III was added to the preheated vaporization flask maintained at 190°C. The nitrogen input rate was 90 ml/min. There was some fogging in the Dewar condenser. Initially, there were some trace amounts of yellow-green product formed near the exit tube. During the first hour of the run, a two-phase mixture was collected. One phase was water. After the first hour the reaction products were homogeneous (one phase) and golden yellow in color. The oven furnace was maintained at 290–320°C. A total of 257.3 grams of reaction products was collected (34.7 grams from the cold trap and 222.6 grams from the Dewar condenser) for a total recovery of 86.9%. The final reaction product distribution in mol % was 78.3% I, 9.6% II, and 84.6% methanol. The conversion of methoxyacetal was 84.7%. The reaction mixture was dried with calcium hydride and distilled. II formed an azeotrope with methanol (bp 64°C, 17.8% II, 82.8% methanol) which was separated by distillation with a slight excess of benzene (*19*). The benzene-methanol azeotrope boiled at 58°C, and a good column is thus required for separation.

General Procedures

Infrared spectra were obtained (with sodium chloride cells) in CCl_4 solvent (1% solution), neat (between sodium chloride disks) or in the gas phase with a 10-cm gas cell (cesium iodide windows) at a pressure of 8 torr. The spectra were obtained on a Perkin-Elmer grating spectrophotometer (Model 457). A normal slit width and medium or slow scan speeds were used. A polystyrene spectrum was used to check the wavelength accuracy. Raman spectra were obtained on a Beckman Model 700 laser Raman spectrometer which employed a He-Ne laser.

All gas chromatograms were run on a Varian 700-A unit with a 10-ft, ¼-in. analytical column containing 25% THEED (tetrahydroxyethyl ethylene diamine) on chromosorb W. The helium flow rate was maintained at 115–120 ml/min. A detector filament current of 150 mA was used at a detector temperature of 210°C. The column oven temperature was maintained at 120° or 100°C. The injection oven temperature was 140°C. Injection quantities were between 1.5 and 2.0 μl for liquids with the voltage attenuator (sensitivity) set at 4× so that components could be kept on the recorder chart.

To measure reaction product distributions for the dealcoholation of methoxyacetal, quantitative vapor-phase chromatography (vpc) techniques were used. A standard was chosen which was always present in high yield as a reaction product. Methanol was chosen as the standard since methanol, methoxyacetal, and the cis- and trans-dimethoxyethylenes were present in the final reaction mixture. This is analogous to the method of internal standards, except that methanol was not weighed in as a standard. A limitation of this technique is the calculation of absolute quantities of reaction products if side reactions occur to an appreciable extent. This was not the case since only small amounts of water formed from the 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.

Acknowledgment

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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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