Polymerization of Vinyl Chloride.—The reactor described above (Dry Ice condenser) was charged with 120 ml. of vinyl chloride, 100 g. of potassium acetate, 600 ml. of water and 100 ml. of ethanol. The electrolysis was conducted for 11.5 hours at 1 ampere. No visible change was noted. The vinyl chloride was allowed to boil off, and the white precipitate of polymer was collected by filtration; yield 0.65 g. The material was not totally soluble in methyl ethyl ketone and 0.15 g. of gel material was filtered off. The intrinsic viscosity of the soluble portion was 0.30 (methyl ethyl ketone, 25°).

Polymerizations with Potassium Acetate-2-C^{14}.—The method of radiocarbon analysis has been described elsewhere.[11] The electrodes (each one inch square of smooth platinum spaced *ca.* $^1/_8$'' apart) were inserted by long leads through the condenser. The reaction mixture consisted of 40 ml. of vinyl acetate, 5 g. of potassium acetate-2-C^{14} (1.209 ± 0.016 mc./mole), and 10 ml. of water. The electrolysis was run with stirring for 15.5 hours at 0.5 ampere. The polymer was recovered as described above. Purification was effected by precipitating the polymer from acetone solution by pouring the latter into water. This process was repeated three times. The yield of polymer was 0.108 g., $[\eta]^{25}$ 0.20 (acetone), radioactivity 3.89 ± 0.09 × 10^{-7} mc./mg.

A measure of the amount of acetate exchange was carried out by stirring a mixture of non-radioactive polyvinyl acetate dissolved in vinyl acetate monomer with a solution of potassium acetate-2-C^{14} made up as nearly as possible as the solution used in the electrolysis experiment. The mixture was stirred at room temperature for three days. The polymer was recovered and purified as above: radioactivity 8.52 ± 0.17 × 10^{-8} mc./mg.

The polymerization of methyl methacrylate was carried out as above but in a 100-ml. flask. A mixture of 15 ml. of methyl methacrylate, 5 g. of potassium acetate-2-C^{14} (1.209 ± 0.016 mc./mole), and 70 ml. of water was electrolyzed at 1.0 ampere for 4.25 hours. The polymer was recovered and purified as above; yield 0.13 g., $[\eta]^{25}$ 0.79 (methyl ethyl ketone), radioactivity 1.18 ± 0.07 × 10^{-6} mc./mg.

ATHENS, OHIO

(11) W. B. Smith, R. E. Bowman and T. J. Kmet, THIS JOURNAL, **81**, 997 (1959).

[CONTRIBUTION NO. 1549 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

1-Methoxyvinyl Esters.[1] I. Preparation and Properties

BY HARRY H. WASSERMAN AND PETER S. WHARTON[2]

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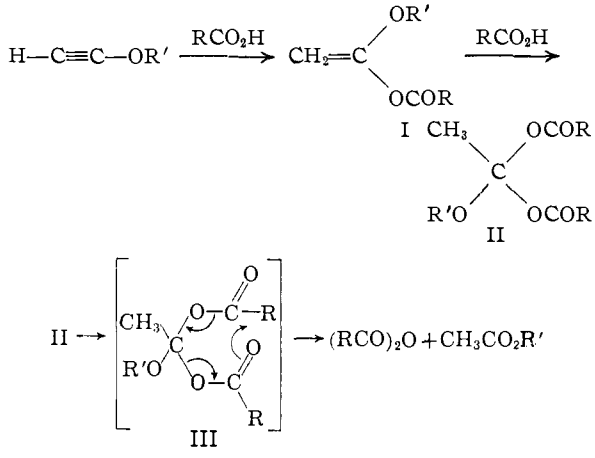
Methods are described for the preparation. in good yield of a number of 1-methoxyvinyl esters from the reaction of methoxyacetylene with the corresponding carboxylic acids. Some of the physical and chemical properties of these compounds are reported.

The reactions of alkoxyacetylenes have been extensively investigated in recent years, mainly by Arens and co-workers.[3] It was found that one mole of methoxy- or ethoxyacetylene reacts rapidly at room temperature with two moles of a variety of carboxylic and other acids to produce the corresponding anhydrides in good yield.[4] This reaction has been assumed to occur by the intermediate formation of 1-alkoxyvinyl esters (I) and 1-alkoxyethylidene diesters (II), anhydride formation resulting from the decomposition of II *via* the cyclic transition state III.[4c]



Early attempts to isolate the intermediate I in the case of the reaction of acetic acid with ethoxyacetylene were unsuccessful using (a) an equimolar amount[4c] and (b) an excess[4a] of ethoxyacetylene. On the other hand, Arens has recently reported the facile formation of I, R = CCl_3, R′ = C_2H_5, as well as I, R = $CHCl_2$, R′ = C_2H_5, from trichloroacetic acid and dichloroacetic acid, respectively, although monochloroacetic acid failed to yield I, R = CH_2Cl, R′ = C_2H_5.[5]

We were interested in methods for the preparation of 1-alkoxyvinyl esters because of their potential usefulness as reactive acylating agents in the synthesis of unsymmetrical anhydrides and peptides.[1] This paper describes our studies with methoxyacetylene.[6]

It was found that 1-methoxyvinyl trifluoroacetate was rapidly formed in good yield (78%) from the reaction of trifluoroacetic acid with a slight excess of methoxyacetylene in methyl chloride solvent. Likewise, in agreement with Arens' findings,[5] 1-methoxyvinyl trichloroacetate appeared

(1) For a preliminary communication on this subject, see H. H. Wasserman and P. S. Wharton, *Tetrahedron*, **3**, 321 (1958). This paper is abstracted from the Doctoral Dissertation of P. S. Wharton, submitted to the Graduate School of Yale University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, June, 1959.

(2) Procter and Gamble Fellow, 1957–1958.

(3) See J. F. Arens and H. C. Volger, *Rec. trav. chim.*, **77**, 1170 (1958), and earlier papers in this series.

(4) (a) J. F. Arens and P. Modderman, *Proc. Koninkl. Ned. Akad. Wetenschap.*, **53**, 1163 (1950); *C. A.*, **45**, 6152 (1951); (b) J. F. Arens and T. Doornbos, *Rec. trav. chim.*, **74**, 79 (1955); (c) G. Eglinton, E. R. H. Jones, B. L. Shaw and M. C. Whiting, *J. Chem. Soc.*, 1860 (1954).

(5) R. Broekema, S. van der Werf and J. F. Arens, *Rec. trav. chim.*, **77**, 258 (1958).

(6) An improved preparation of methoxyacetylene on a two-molar scale, by a modification of the published procedure for ethoxyacetylene, *Org. Syntheses*, **34**, 46 (1954), is described in detail in the Experimental section. See also the procedure for the preparation of ethoxyacetylene described by I. N. Nazarov, Zh. A. Krasnaia and V. P. Vinogradov, *J. Gen. Chem. U.S.S.R.*, **28**, 451 (1958).

to form readily in ether and methylene chloride solutions at room temperature. In contrast, the reaction of approximately equimolar amounts of acetic acid and methoxyacetylene in the absence of solvent, led only to acetic anhydride, thus corroborating the earlier work.[4a,4c,7] It was shown, however, that a small amount (5%) of 1-methoxyvinyl acetate was formed at room temperature in methylene chloride when the concentration of each reactant was 2.5 molar, and that more (35%) was produced at higher dilution (0.1 molar).[8] However, at these dilutions, the reactions took two and ten days, respectively, to go to completion. By the use of a large excess of methoxyacetylene the reaction time was shortened and 1-methoxyvinyl acetate was obtained in good yield. From the above results it appears that increasing the strength of the acid, diluting the reaction medium and using an excess of alkoxyacetylene all favor the formation of the intermediate I.

In the case of every acid studied, listed below, it was found that one could prepare the desired intermediates (I) in good yield by using a sufficiently large excess of methoxyacetylene. The amount of methoxyacetylene actually used varied from a slight excess with trifluoroacetic acid to a nearly fifty-fold excess with acetic acid. On a small scale, the use of such large excesses of methoxyacetylene is not disadvantageous as the reagent can readily be recovered and used again.

Another procedure which was particularly useful on a large scale employed the known catalytic effect of mercuric ions on reactions involving addition to the acetylenic linkage. For preparative purposes the acid (1 mole) was treated with methoxyacetylene (2 to 3 moles) in dilute methylene chloride (*ca.* 0.1 molar in acid) in the presence of a mercuric salt (0.02 mole), preferably the salt of the acid used. Under these conditions, only very small amounts of the corresponding anhydrides were formed and the yields of 1-methoxyvinyl esters, obtained after removing the catalyst and any anhydride by distillation or crystallization, ranged from 66 to 98%. The acids thus treated were acetic, 3β-acetoxy-Δ^5-bisnorcholenic, chlorodiphenylacetic, benzoic, *p*-nitrobenzoic, 3,5-dinitrobenzoic and *p*-phenylazobenzoic, the last of which failed to react at all in the absence of mercuric ions, presumably because of its insolubility in the solvent.

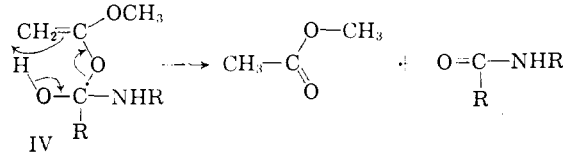
We have not as yet investigated the limitations imposed on this reaction by the presence of other functional groups, although there is evidence that weakly basic groups such as –OH and pyrrole–NH do not cause interference. Thus the infrared spectra of reaction mixtures of methoxyacetylene with benzilic acid, 3β-hydroxy-Δ^5-cholenic acid and pyrrole-2-carboxylic acid show, in each case, the bands at *ca.* 5.65 and 5.95 μ characteristic of the 1-methoxyvinyl ester system.

Treatment of formic acid with methoxyacetylene in the presence of mercuric oxide showed, spectroscopically, that 1-methoxyvinyl formate was produced. However, the methylene chloride solution decomposed at room temperature with the evolution of a gas (presumably carbon monoxide) and, on distillation, only methyl acetate was recovered. This facile decomposition of 1-methoxyvinyl formate may occur intramolecularly or, more probably, by the action of traces of formic acid on the ester to form formic anhydride, the spontaneous decomposition of the latter producing carbon monoxide and regenerating formic acid.

The structure of the esters follows from their mode of formation, and is supported by the presence of two intense bands in the 5 to 6 μ region of the infrared. The band at *ca.* 5.61 μ (acetate) or 5.75 μ (benzoate) is characteristic of the >C=O stretching in an enol ester, and the peak at *ca.* 5.95 μ can be ascribed to the >C=CH_2 stretching. In 1-substituted vinyl acetates[9] and ketene acetals,[10] for example, the latter band appears at approximately 6.0 μ.

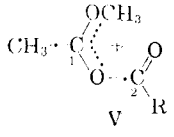
In the ultraviolet, 1-methoxyvinyl acetate shows no absorption above 210 mμ with an ε greater than 200. Sealed samples of this ester, stored at 5°, showed no tendency to polymerize or decompose over a period of several months.

As expected, 1-methoxyvinyl esters are active acylating agents. Benzylamine reacted vigorously with I, R = CH_3, R′ = CH_3, at room temperature and amides were readily obtained from other 1-methoxyvinyl esters. The weaker bases, β-naphthylamine and *p*-nitrobenzyl alcohol, were acetylated less readily and, in fact, some 1-methoxyviny lesters could be crystallized from alcohol. The acylation of such bases presumably occurs by the initial addition of the base to the carbonyl carbon atom of the ester, the subsequent decomposition proceeding with an inter- or intramolecular proton transfer, *e.g.*, IV.



IV

Acid-catalyzed acylations were also observed. Hydrogen chloride, for example, reacted almost instantaneously with 1-methoxyvinyl chlorodiphenylacetate, in dilute hexane solution, to produce the corresponding acid chloride. Similarly, the weaker acid, 2,4-dinitrophenol, was acylated, although slowly. Such acylations presumably proceed by initial protonation of the 1-methoxyvinyl ester to form the ion V which may be at-



V

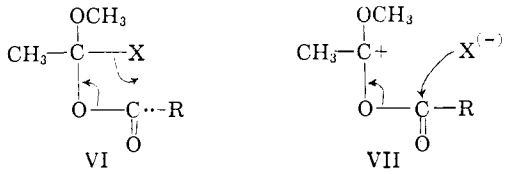
(7) This apparently striking difference in behavior between weak and strong acids is explained in a subsequent paper; see H. H. Wasserman and P. S. Wharton, THIS JOURNAL, in press.

(8) The effect observed on increasing the dilution is to be expected if protonation is rate-determining in the formation of 1-alkoxyvinyl esters but is not rate-determining in the subsequent reaction. Under these conditions, the rate of formation of 1-alkoxyvinyl ester I must be directly proportional to the acid concentration, whereas the rate of conversion of I to II must be proportional to the square of the acid concentration.

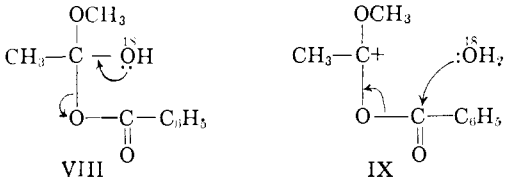
(9) H. Vanderhaeghe, E. R. Katzenellenbogen, K. Dobriner and T. F. Gallagher, THIS JOURNAL, **74**, 2810 (1952).

(10) S. M. McElvain and R. E. Starn, Jr., *ibid.*, **77**, 4571 (1955).

tacked by a nucleophile X at either of the positively charged carbon atoms, C-1 or C-2. *A priori*, it is more likely that the faster reaction would be addition to the more positive center at C-1, resulting in the formation of an orthoester derivative. The acylation of X might then result from an intramolecular four-membered transition state VI, or from the ready, reversible dissociation of the orthoester, followed by addition of the nucleophile to the carbonyl carbon atom (VII).



Evidence that addition to the 1-vinyl carbon atom (C-1) is faster than addition to the carbonyl carbon atom was found in the acid-catalyzed reaction of water with 1-methoxyvinyl benzoate. In the absence of added acid the reaction was very slow. Benzoic acid was, however, formed quantitatively in about two hours at room temperature from a reaction mixture of the benzoate and a large excess of 0.1 *N* hydrochloric acid. When the reaction was run with 0.1 *N* acid containing 1.27 atom per cent. excess O^{18}, the benzoic acid which was recovered contained only 0.12 atom per cent. excess O^{18}, less than 10% of the excess originally present in the water. It can, therefore, be inferred that, subsequent to protonation, water adds faster to the 1-vinyl carbon atom than to the carbonyl carbon atom. As illustrated below, these two modes of addition would lead to benzoic acid containing, in the case of VIII, *none*, or in the case of IX, *all* of the excess O^{18} present in the water. The origin of the small amount of excess O^{18} found in the recovered benzoic acid was not investigated.



Experimental[11]

Methoxyacetylene.—*Caution! Because of the large amounts of sodium and sodium methoxyacetylide involved in this preparation, special precautions should be taken to ensure safety during the experiment. The preparation should be conducted in a well-vented hood to avoid exposure to ammonia.*

Three liters of liquid ammonia was introduced into a 5-l. three-necked flask, fitted with a stirrer and a Dry Ice condenser connected to a soda-lime tube. (The use of rubber stoppers facilitates the manipulation of the joints when cold.) After adding 2.5 g. of hydrated ferric nitrate, 180 g. of sodium was dissolved with stirring. The top half of the flask was then washed with a spray of liquid ammonia to make sure that no unreacted sodium remained as the presence of minute specks of unreacted sodium makes the quenching of the sodium salt of methoxyacetylene hazardous. The contents of the flask were stirred for 1 to 2 hours, and more ammonia added to keep the volume at 1500 ml. The stirrer was removed and the flask transferred to the free lower end of a 30-inch flexible metal rod, the upper end of which was clamped securely to a crossbar. After flushing the flask with more liquid ammonia, dimethylchloroacetal (311 g.), b.p. 126–130°, was added gradually during 30 minutes from a 1-l. addition funnel. (Incautious addition of the acetal results in an uncontrollably violent reaction.) The flask was swirled by hand throughout the addition, and the swirling continued for an additional 15 minutes. Solid on the sides of the flask was flushed down with liquid ammonia, and the Dry Ice condenser removed. Prepurified nitrogen was passed slowly through the flask, and the ammonia allowed to evaporate over 40 hours. The flask was then cooled to −70° while increasing the nitrogen flow, and the sodium methoxyacetylide quenched as rapidly as possible with a solution of 2 lb. of calcium chloride dihydrate in 1300 ml. of water, cooled to −45°. A convenient apparatus which enables the calcium chloride solution to be added in less than 5 seconds consists of a 3-l. flask with a short exit tube of 19 mm. diameter sealed to the bottom. A 5-inch length of soft rubber tubing which is clamped, connects the two flasks. After the cold calcium chloride solution had been added to the 3-l. flask, nitrogen, not prepurified, was passed over it to prevent the entrance of air into the system, and the clamp was quickly released. The reaction flask was well shaken, transferred to a firm stand, and the methoxyacetylene distilled through a short Vigreux column into a Dry Ice-cooled 1-l. three-necked flask, fitted with a stirrer and a Dry Ice condenser. The 5-l. flask was first allowed to warm to room temperature, and then heated slowly with a heating mantle until the distillation temperature reached 60°. The distillate (*ca.* 125 g.) was allowed to warm to 0°, whereupon 600 ml. of ice-cold heptane was added with stirring, and the ammonia present in the distillate neutralized with a saturated solution of sodium dihydrogen phosphate (end-point detected with phenolphthalein). (Very little, *ca.* 20 drops, of sodium dihydrogen phosphate solution is needed if the preparation has been successful.) The aqueous layer was frozen out at about −50° (cooling below this temperature results in the separation of two liquid phases) and the organic layer decanted and dried over 11 g. of anhydrous calcium chloride. After filtration, the solution was distilled through a simple column (three to four plates) to yield 109 g. (78%) of methoxyacetylene, b.p. 22.5–24.0°, $n^{16}D$ 1.3697.

1-Methoxyvinyl Trifluoroacetate.—Trifluoroacetic acid (4.75 ml., 7.22 g., 0.063 mole) was added over 40 minutes to a stirred solution of 5.0 ml. (0.071 mole) of methoxyacetylene in *ca.* 50 ml. of methyl chloride. (The initially colorless solution became increasingly orange as the acid was added.) After the solvent had been allowed to evaporate, the infrared spectrum of the reaction product showed that the resulting 1-methoxyvinyl trifluoroacetate was contaminated with small amounts of materials(s) absorbing at 5.74 μ. No anhydride was observable. Distillation of the liquid under reduced pressure gave 8.40 g. (78%) of 1-methoxyvinyl trifluoroacetate, b.p. 49.5–51.0° (136 mm.), $n^{25}D$ 1.3391. The residue consisted of 0.5 ml. of a red mobile liquid which contained relatively more of the component(s) absorbing at 5.74 μ. Analytical 1-methoxyvinyl trifluoroacetate was obtained from the middle fraction of the distillate in another run, b.p. 32° (55 mm.), $n^{25}D$ 1.3389, 5.52 and 5.93 μ (CCl_4).

Anal. Calcd. for $C_5H_5F_3O_3$: C, 35.31; H, 2.96. Found: C, 35.68; H, 3.07.

Attempted Preparation of 1-Methoxyvinyl Formate.—Methoxyacetylene (17 ml., 0.24 mole) was added with stirring to a suspension of 0.594 g. (0.0027 mole) of mercuric oxide in 180 ml. of dry, ice-cooled methylene chloride. A solution of 5.2 g. (0.113 mole) of formic acid (99%) in 50 ml. of the same solvent was added slowly to the solution, the temperature of which was maintained at 0–5°. The infrared spectrum of the reaction solution, which decomposed at room temperature with the evolution of a gas, showed the formation of 1-methoxyvinyl formate (5.63 and 5.95 μ) and methyl acetate (5.74 μ). Fractionation of the solution (oil-bath at 60–70°) yielded only methyl acetate, b.p. 54.5–57.0°. There was a negligible residue.

1-Methoxyvinyl Acetate.—Methoxyacetylene (35 ml., 0.50 mole) was added with stirring to a suspension of 1.50 g. (0.0047 mole) of mercuric acetate in 460 ml. of dry, ice-

(11) All b.p.'s and m.p.'s are uncorrected. The latter were determined in soft glass capillary tubes in a Hershberg apparatus. Microanalyses by Schwarzkopf Microanalytical Laboratories, 56-19 37th Ave., Woodside 77, N. Y. Infrared spectra were recorded on a Perkin-Elmer model 21 spectrophotometer, calibrated against the spectrum of the atmosphere.

cooled methylene chloride. To the resulting clear, pale yellow solution, a solution of glacial acetic acid (14.63 ml., 15.35 g., 0.256 mole) in 30 ml. of the same solvent was added over 30 minutes. The solvent and excess methoxyacetylene were then removed (and condensed for subsequent use) by heating in an oil-bath at 70–80°. The dark yellow residue was distilled under reduced pressure through a simple spiral column (two to three plates) to give 27.2 g. (92%) of crude 1-methoxyvinyl acetate, b.p. 83° (100 mm.), $n^{25}D$ 1.4109, containing approximately 5% acetic anhydride as determined by infrared analysis. The product was dissolved in 90 ml. of dry pentane at 0°, and freshly prepared sodium methoxide was added in 200-mg. portions every hour, with continuous stirring, until no anhydride remained. This was most conveniently determined by observing the disappearance of the 8.9 μ band of the anhydride in the infrared spectrum of the pentane solution. A product containing less than 0.1% anhydride was easily obtained. In practice, 600–800 mg. of methoxide was added over 4 to 6 hours. The solution was filtered, the solvent removed, and the residue distilled under reduced pressure to give 21.7 g. (73%) of pure 1-methoxyvinyl acetate, b.p. 142.5–143.5° with yellowing, 79° (85 mm.), $n^{25}D$ 1.4122, d^{25} 1.0827, R_D 28.1 (calcd. 28.1), 5.61 and 5.95 μ (CCl_4).

Anal. Calcd. for $C_5H_8O_3$: C, 51.72; H, 6.94. Found: C, 51.80; H, 6.84.

Acetylation with 1-Methoxyvinyl Acetate. A. Benzylamine.—Benzylamine (17.8 mg., 0.17 mmole) and 22 mg. (0.19 mmole) of 1-methoxyvinyl acetate were added dropwise to a small culture tube. After the vigorously exothermic reaction, the volatiles were removed to give 24.9 mg. (100%) of N-benzylacetamide, m.p. 58–60°. Crystallization from methanol raised the m.p. to 64–65°.

B. **β-Naphthylamine.**—A solution of 50.0 mg. (0.35 mmole) of β-naphthylamine and 50 mg. (0.43 mmole) of 1-methoxyvinyl acetate in 0.5 ml. of methylene chloride was heated for two hours at 80°. The volatiles were then removed to give 64.9 mg. (100%) of N-β-naphthylacetamide, m.p. 130–131°, 5.94 μ ($CHCl_3$). Crystallization from methanol raised the m.p. to 131–132°.

C. **2,4-Dinitrophenol.**—A solution of 48.0 mg. (0.26 mmole) of 2,4-dinitrophenol and 36 mg. (0.31 mmole) of 1-methoxyvinyl acetate in 0.5 ml. of methylene chloride was allowed to stand at room temperature for 8 hours. Removal of the volatiles gave 58.6 mg. (99%) of 2,4-dinitrophenyl acetate, m.p. 71–72°, 5.60 μ ($CHCl_3$). Crystallization from methanol gave 55 mg. (93%), m.p. 71.9–72.4°.

D. **p-Nitrobenzyl Alcohol.**—A mixture of 25.3 mg. (0.17 mmole) of p-nitrobenzyl alcohol and 40 mg. (0.34 mmole) of 1-methoxyvinyl acetate was heated at 80° for three hours. Removal of the volatiles gave 31.9 mg. (99%) of p-nitrobenzyl acetate, m.p. 75–78°. Crystallization from methanol raised the m.p. to 78.6–79.1°.

1-Methoxyvinyl Benzoate.—Methoxyacetylene (20 ml., 0.29 mole) was added to a suspension of 1.50 g. (0.0034 mole) of mercuric benzoate (prepared by fusing equivalent amounts of mercuric oxide and benzoic acid) in 450 ml. of dry, ice-cooled methylene chloride. To the resulting clear yellow solution, a solution of 19.5 g. (0.16 mole) of benzoic acid in 170 ml. of methylene chloride was added over 40 minutes with stirring. After a further 20 minutes, the solution was heated in an oil-bath at 80° and the solvent and excess methoxyacetylene removed (and condensed for subsequent use). The residue was transferred to a 50-ml. flask and distilled through a small spiral column (two to three plates) to give 28.0 g. (98%) of 1-methoxyvinyl benzoate, b.p. 95–96° (0.5 mm.), $n^{25}D$ 1.5181, 5.70 and 5.96 μ (CCl_4).

Anal. Calcd. for $C_{10}H_{10}O_3$: C, 67.40; H, 5.66. Found: C, 67.69; H, 5.78.

Benzoylation with 1-Methoxyvinyl Benzoate. A. Benzylamine.—Benzylamine (18.3 mg., 0.17 mmole) and 37 mg. (0.21 mmole) of 1-methoxyvinyl benzoate were mixed in a small culture tube. After five minutes, volatiles were removed to give 35.3 mg. (98%) of N-benzylbenzamide, m.p. 105.8–106.2°, unchanged after crystallization.

B. **2,4-Dinitrophenol.**—A mixture of 66.8 mg. (0.36 mmole) of 2,4-dinitrophenol and 78 mg. (0.44 mmole) of 1-methoxyvinyl benzoate was heated at 80° for 1.5 hours. Volatiles were removed and the dark brown solid was washed with a little cold methanol to give 80 mg. (76%) of 2,4-dinitrophenyl benzoate, m.p. 130–132°. Crystallization from ethyl acetate raised the m.p. to 131–132°.

C. **Water-O^{18}.**—A two-phase system of 165 mg. (0.93 mmole) of 1-methoxyvinyl benzoate and 116 mg. of 0.13 *N* hydrochloric acid, containing 1.47 atom per cent. O^{18}, was shaken in a sealed tube for 150 minutes at 22°. After centrifuging, the tube was opened and the volatiles removed to give a residue of pure benzoic acid, m.p. 122–123°, containing 0.26 atom per cent. O^{18} per oxygen.

1-Methoxyvinyl Chlorodiphenylacetate. With Hg^{++}.—A solution of 247 mg. (1 mmole) of chlorodiphenylacetic acid in 5 ml. of dry methylene chloride was added over 15 minutes at room temperature to a solution of 0.18 ml. (2.6 mmoles) of methoxyacetylene in 10 ml. of methylene chloride, containing 6.1 mg. (0.019 mmole) of mercuric acetate. After standing for 30 minutes, the volatiles were removed to give an oil which slowly crystallized; yield of crude ester, 303 mg. (98%), m.p. 56–62°. The solid (42 mg.) was dissolved in benzene, hexane added, and the small amount of precipitated solid removed by centrifugation. After evaporation of the solvent, the product was crystallized from a small volume of 4:1 hexane–benzene by first cooling slowly to 5°, with seeding to prevent oiling out, and then leaving at −20° overnight; yield 30 mg. (70%), m.p. 61–63°, 5.61 and 5.65 μ doublet and 5.96 μ (CCl_4). Further crystallization from 3:1 hexane–benzene gave analytical material, m.p. 63–63.5°.

Anal. Calcd. for $C_{17}H_{15}ClO_3$: C, 67.44; H, 4.92; Cl, 11.71. Found: C, 67.54; H, 4.95; Cl, 11.49.

Without Hg^{++}.—A solution of 500 mg. (2.03 mmoles) of chlorodiphenylacetic acid in 10 ml. of methylene chloride, containing 1 ml. (14 mmoles) of methoxyacetylene, was left overnight. Removal of the volatiles gave an oil which slowly crystallized; yield 600 mg. (98%), m.p. 58–61° (mainly), clearing at 64°. The crude product (418 mg.) was crystallized (two hours at 5°) from 1.2 ml. of a 3:1 hexane–benzene mixture to give 160 mg. (38%) of purified ester, m.p. 61–63°. The filtrate was concentrated, hexane added, and the solution left overnight at room temperature to give a further 120 mg. (28%), m.p. 60–63°.

Chlorodiphenylacetyl Chloride.—Dry hydrogen chloride was bubbled through a solution of 24 mg. (0.079 mmole) of 1-methoxyvinyl chlorodiphenylacetate in 2 ml. of dry hexane. Removal of the volatiles gave an oil which slowly crystallized; yield of almost pure chlorodiphenylacetyl chloride, 21 mg. (100%), m.p. 50–52°. Crystallization from pentane at 5° raised the m.p. to 51.5–53°. A small amount of an impurity, not removed by crystallization, absorbing at 5.81 μ (CCl_4), was evident in the infrared spectrum of the product. When the reaction was run at higher dilution, relatively less of this impurity was formed, and it is probable that it was polymeric 1-methoxyvinyl chlorodiphenylacetate.

1-Methoxyvinyl 3β-Acetoxy-Δ^5-bisnorcholenate. With Hg^{++}.—A solution of 388 mg. (1 mmole) of 3β-acetoxy-Δ^5-bisnorcholenic acid in 10 ml. of methylene chloride, containing 0.18 ml. (2.6 mmoles) of methoxyacetylene and 6.5 mg. (0.020 mmole) of mercuric acetate, was allowed to stand at room temperature. After one hour, the infrared spectrum of the solution showed that much acid had not reacted, and the solution was left overnight. Removal of the volatiles gave 444 mg. (99%) of crude ester, m.p. 127–136°. Crystallization of 73 mg. from 1 ml. of dry methanol at −20° (after centrifuging from a small amount of insoluble matter) gave 63 mg. (85%) of purified ester, m.p. 134–136.5°; 5.68, 5.76 and 5.94 μ (KBr). The dissolution in hot methanol and subsequent centrifugation were done rapidly to minimize decomposition of the ester. Analytical material was obtained after two more crystallizations from the same solvent, m.p. 136.5–137.5°.

Anal. Calcd. for $C_{27}H_{40}O_5$: C, 72.94; H, 9.07. Found: C, 73.32; H, 9.09.

Without Hg^{++}.—A solution of 500 mg. (1.29 mmoles) of 3β-acetoxy-Δ^5-bisnorcholenic acid and 1 ml. (14 mmoles) of methoxyacetylene in 10 ml. of methylene chloride was left overnight at room temperature. Removal of the volatiles gave 572 mg. (100%) of almost pure ester, m.p. 132.5–136°. Crystallization of 97 mg. from 1.5 ml. of dry methanol at 5° gave 79 mg. (81%) of purified ester, m.p. 134.5–136.5°.

3β-Acetoxy-Δ^5-bisnorcholenic Acid Amide.—A tube containing 55 mg. (0.12 mmole) of 1-methoxyvinyl 3β-ace-

toxy-Δ^5-bisnorcholenate, 0.1 ml. of absolute ethanol and 0.1 ml. of liquid ammonia was sealed and then heated at 68° for two hours. The tube was opened and the volatiles removed to give 48 mg. (100%) of the amide,[12] m.p. 221–226°; 5.77, 6.02, and 6.09 μ (KBr). Crystallization of 6 mg. from methanol at 5° gave 5 mg. (80%), m.p. 226–227°.

Attempts to prepare the diethylamide were unsuccessful. The reaction was incomplete after heating the ester with diethylamine for two hours at 140° in a sealed tube; after 12 hours, no ester remained but ammonolysis of the acetate group seemed to have occurred to a considerable extent.

1-Methoxyvinyl *p*-Nitrobenzoate. With Hg^{++}.—*p*-Nitrobenzoic acid (167 mg., 1 mmole), 0.3 mg. (0.001 mmole) of mercuric acetate and 2.8 mmoles of methoxyacetylene in 2 ml. of methylene chloride were stirred together at room temperature for one hour. The acid is not very soluble in the solvent and the end of the reaction was evident when the solution clarified. Removal of the volatiles gave 215 mg. (96%) of crude 1-methoxyvinyl *p*-nitrobenzoate, m.p. 67–72°, containing a little anhydride, 5.54 μ (CH_2Cl_2). The crude ester (130 mg.) was dissolved in 4 ml. of hot ethanol and the solution cooled rapidly and allowed to stand at room temperature for five minutes, after which it was centrifuged from the small amount of deposited solid. The clear filtrate was stored at −20° and gave 89 mg. (66%) of long, pale yellow needles, m.p. 75–78°, 5.72 and 5.94 μ (KBr). A further crystallization from ethanol gave analytical material, m.p. 76.5–78°.

Anal. Calcd. for $C_{10}H_9NO_5$: C, 53.81; H, 4.06; N, 6.28. Found: C, 53.72; H, 4.28; N, 6.36.

***p*-Nitrobenzamide.**—A tube containing 37.8 mg. (0.17 mmole) of 1-methoxyvinyl *p*-nitrobenzoate, m.p. 75–78°, 0.2 ml. of absolute ethanol and 0.2 ml. of liquid ammonia was sealed, heated momentarily to dissolve the solid, and then left at room temperature for 10 minutes. Removal of the volatiles gave 28.2 mg. (100%) of crude amide, m.p. 192–199°. Crystallization of 5.4 mg. from 0.5 ml. of water at 5° gave 4.6 mg. (85%), m.p. 198–202°, raised to 201–202.5° by a further crystallization; 6.01 μ (KBr).

1-Methoxyvinyl 3,5-Dinitrobenzoate.—A suspension of 217 mg. (1.02 mmoles) of 3,5-dinitrobenzoic acid in 1.8 ml. of methylene chloride, containing 0.9 mg. (0.0028 mmole) of mercuric acetate and 2.5 mmoles of methoxyacetylene, was stirred at room temperature. The reaction was complete in 12 minutes (evident from the clearing of the solution). Removal of the volatiles gave 267 mg. (97%) of crystalline 1-methoxyvinyl 3,5-dinitrobenzoate, m.p. 93.5–95.5°, containing only small amounts of anhydride, *ca.* 5.5 μ (CH_2Cl_2). Attempts to crystallize the ester led to extensive decomposition. Analytical material was obtained in another run, using 106 mg. (0.5 mmole) of acid and 7 mmoles of methoxyacetylene in 5 ml. of methylene chloride (no mercuric salt was added). The reaction was complete in 15 minutes. Removal of the volatiles gave 135 mg. (101%) of crystalline ester, 93.5–95.5°, 5.71 and 5.94 μ (KBr).

Anal. Calcd. for $C_{10}H_8N_2O_7$: C, 44.78; H, 3.01; N, 10.45. Found: C, 45.03; H, 3.24; N, 10.29.

1-Methoxyvinyl *p*-Phenylazobenzoate. With Hg^{++}.—A suspension of 41 mg. (0.18 mmole) of *p*-phenylazobenzoic acid in 3 ml. of methylene chloride, containing 0.8 mmole of methoxyacetylene, was stirred at room temperature for 12 hours. The infrared spectrum of the filtered solution showed that the acid was sparingly soluble in the solvent and negligible reaction had occurred. After the addition of 2.7 mg. (0.0085 mmole) of mercuric acetate, the reaction proceeded rapidly and was complete in half an hour (evident from the clearing of the solution). Removal of the volatiles gave 51 mg. (96%) of crude 1-methoxyvinyl *p*-phenylazobenzoate, m.p. 76–80°. With rapid heating and cooling of the solution, 32 mg. was crystallized from ethanol at 5° to give 26.5 mg. (80%) of pure ester, 5.72 and 5.97 μ (KBr). If heated slowly from 70°, a transition with partial melting, followed by solidification, occurred at 81°, m.p. (sharp) 94.5–95.5°. If immersed in the oil-bath at 85°, the ester melted completely before solidifying and finally remelting at 94.5–95.5°.

Anal. Calcd. for $C_{16}H_{14}N_2O_3$: C, 68.07; H, 5.00; N, 9.92. Found: C, 68.03; H, 5.09; N, 9.94.

***p*-Phenylazobenzamide.**—A tube containing 6.0 mg. (0.021 mmole) of 1-methoxyvinyl *p*-phenylazobenzoate, 0.2 ml. of ethanol and 0.1 ml. of liquid ammonia was sealed and left at room temperature for 10 minutes. Removal of the volatiles gave 4.9 mg. (100%) of amide, m.p. 226–227°, unchanged after crystallization from ethanol; 6.04 μ (KBr).

1-Methoxyvinyl 3β-Hydroxy-Δ^5-cholenate. Without Hg^{++}.—A suspension of 53 mg. (0.14 mmole) of 3β-hydroxy-Δ^5-cholenic acid in 5 ml. of methylene chloride was stirred overnight with 0.4 ml. (5.7 mmoles) of methoxyacetylene. Removal of the volatiles gave 61 mg. (100%) of crude ester, m.p. 125–127° (capillary tube inserted at 120°), 5.70 and 5.96 μ (KBr). An attempt to crystallize the crude material from methanol resulted in crystals melting less sharply below 110°. The crude product was not further characterized.

NEW HAVEN, CONN.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE UNIVERSITY OF NORTH CAROLINA AND OF BROWN UNIVERSITY]

The Mechanism of Aminolysis of Esters[1,2]

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The reaction of ethyl formate with *n*-butylamine in ethanol solution to form *n*-butylformamide is general base catalyzed. The rate law contains terms second order in amine (representing amine catalysis) and 3/2 order in amine (representing alkoxide ion catalysis) but no detectable term first order in amine. Addition of *n*-butylammonium chloride affects the rate law and the rate in a fashion consistent with this interpretation. The results are best represented by the mechanism of equations 23–25. The mechanism of equations 1–4, formerly generally accepted, is untenable. This work constitutes additional evidence for the intermediate complex mechanism as a general mechanism for substitution at carbonyl carbon.

The reactions of carboxylic esters with amines to form carboxamides have been extensively studied.[3,4] Careful kinetic researches[5,6] have revealed that such reactions are susceptible to base catalysis.

Ester aminolyses are in the category of nucleophilic substitutions at unsaturated carbon. An-

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