TABLE III
ANALYTICAL RESULTS

Compound	Calcd. C	Calcd. H	Calcd. N	Calcd. P	Found C	Found H	Found N	Found P
VII, $C_{21}H_{16}NO_3P$	69.80	4.43	3.88	8.60	69.31	4.18	3.85	8.64
VIII, $C_{16}H_{14}NO_4P$	61.10	4.48	4.45	9.84	61.25	3.94	4.45	9.88
IX, $C_{17}H_{16}NO_4P$	61.99	4.33	4.48	9.54	62.00	4.86	4.25	9.43
X, $C_{24}H_{17}N_2O_6P$	62.70	3.74	6.10	6.73	62.67	4.00	5.97	7.13
XI, $C_{15}H_{12}NO_4P$	59.90	4.03	4.66	10.29	59.74	3.97	4.75	10.87
XII, $C_{12}H_{14}NO_4P$	53.93	5.28	5.24	11.59	53.40	4.78	5.05	11.20
XIII, $C_{10}H_{10}NO_4P$	50.22	4.21	5.86	12.95	49.90	4.44	6.44	12.40
XV, $C_{13}H_{14}NOP$	67.50	6.15	6.06	13.38	67.54	6.23	5.40	13.38
XVI, $C_7H_{10}NO_2P$	49.06	5.85	8.18	18.10	49.10	5.83	8.30	17.70
XVII, $C_2H_8NO_2P$	22.02	7.39	12.84	28.41	22.00	6.80	12.71	28.28
XVIII, $C_8H_{12}NO_2P$	51.89	6.54	7.76	16.73	51.35	6.25	7.75	16.24

TABLE IV
INFRARED ABSORPTIONS (CM.$^{-1}$) AND ASSIGNMENTS

Compound	
XII	1035 (P–O–C), 1215 (P ⟶ O), 1712 [C(O)N]
XIII	1244 (P ⟶ O), 1715 [C(O)N], 2632 (P–OH)
XV	996 (P–C_6H_5), 1186 (P ⟶ O), 1439 (P–C_6H_5), 3268 and 3322 (NH_2)
XVI	998 (P–C_6H_5), 1130 and 1170 (P ⟶ O), 1439 (P–C_6H_5), 2353 to 2500 (zwitterion character), 2597 (P–OH), 3125 to 3333 (H-bonding)
XVII	1136 and 1156 (P ⟶ O), 2353 to 2500 (zwitterion character), 2597 (P–OH)
XVIII	996 (P–C_6H_5), 1131 and 1156 (P ⟶ O), 1439 (P–C_6H_5), 2353 to 2500 (zwitterion character), 2597 (P–OH)

48% aqueous hydrobromic acid. The phthalic acid formed was filtered off at 5–20°, and the filtrate was evaporated *in vacuo* to remove water and excess hydrogen bromide. Treatment of the crude hydrobromides so formed with hydrogen bromide acceptors under the conditions given in Table II led to crude products which were isolated and purified as shown.

If the hydrolysis of VIII or XII was stopped after 10–30 min., the precipitate present proved to be XI or XIII, respectively, *i.e.*, only the ester group was selectively hydrolyzed first. The precipitates were recovered and purified as shown in Table II.

Analytical data for the products in Table II are listed in Table III; infrared in Table IV.

Acknowledgment.—This work was supported in part by the Office of Naval Research. Analytical work was performed by our analytical department, including the interpretation of the infrared spectra by Miss Ruth A. Kossatz. Miss Barbara I. D'Iorio assisted in part of the experimental work.

A New Synthesis of 1,1,4,4-Tetramethoxybutyne-2

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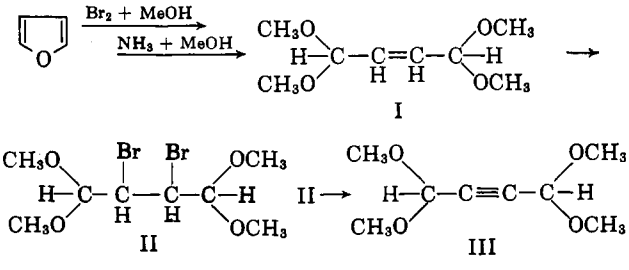
During a program initiated to investigate alkoxy-substituted unsaturates, tetramethoxybutyne was synthesized. This compound had previously been prepared by Wohl[1] *via* the reaction of acetylene di-Grignard and methyl orthoformate. This route has very stringent reaction conditions, and generally requires extreme care during work-up before isolation of the final product. The new synthesis has the advantage of a simplified preparation in addition to a crystalline intermediate which can be isolated and used as a check on the preceding steps.

The precursor 1,1,4,4-tetramethoxybutene-2 (I) was prepared by brominating furan with one equivalent of bromine in methanol solution to give the 2,5-dimethoxydihydrofuran. Without isolating this intermediate the furan ring was opened by ammonolysis[2] to give the tetramethoxybutene. Bromination of the butene gave a crystalline dibromo derivative II melting at 99–99.5°.



Dehydrobromination of the crystalline dibromo compound could theoretically lose two moles of hydrogen bromide, to give either the butyne, butadiene, or allene derivative. Using potassium *t*-butoxide in *t*-butyl alcohol only the butyne III was isolated. (Alcoholic potassium hydroxide gave the same results.) The partially dehydrobrominated product, 1,1,4,4,-tetramethoxy-2-bromobutene-2, was not found as a reaction product.

A sample of the butyne prepared by this new method was compared with that produced by Wohl's synthesis[1], and they were found to be identical.

(1) A. Wohl and E. Bernreuther, *Ann.*, **481**, 1 (1930).

(2) A. Boehringer, E. Boehringer, I. Liebrecht, and J. Liebrecht, British Patent 747,281 (January 25, 1954).

Experimental

1,1,4,4-Tetramethoxybutene-2 (I).—A 2-l. three-necked flask was charged with 90.6 g. (1.33 moles) of dry furan, 334 ml. of absolute methanol, and 266 ml. of anhydrous ether. The flask, which was fitted with a mechanical stirrer, thermometer, and addition tube, was cooled to −40° in a Dry Ice–acetone bath. To this stirred solution was slowly added a cooled solution of 214 g. (1.34 moles) of bromine in 666 ml. of absolute methanol. The reaction temperature was allowed to rise to −35°. Reaction temperature was maintained between −40 and −30°. Addition took 1.5 hr. After addition was completed the reaction temperature was maintained at −35° for 30 min. and then it was raised to −19°. Anhydrous ammonia was bubbled through (addition tube removed and gas inlet tube inserted) the reaction. The temperature was kept between −19° and −10°. The clear yellow solution turned opaque and then white in 15 min. (pH 2, universal indicator paper). Ammonia addition was continued until pH 7+ was reached. Total time for ammonia addition was 1 hr.

The reaction mixture was filtered. The precipitate was washed with ether and refiltered. The filtrates were combined and poured into a saturated sodium chloride solution. This was then extracted with ether several times until the ether extract was nearly colorless. The combined ether layers were dried over anhydrous magnesium sulfate, filtered and then distilled (atm.) to remove the ether and methanol. The residue was vacuum distilled. The product distilled at 95–100° (15 mm.) as a pale yellow liquid. N.m.r. gave a correct proton ratio of 1:1:6.

Anal. Calcd. for $C_8H_{16}O_4$: C, 54.5; H, 9.09. Found: C, 54.9; H, 8.88.

1,1,4,4-Tetramethoxy-2,3-dibromobutane (II).—A 1-l. four-necked flask fitted with a stirrer, addition tube, and thermometer was set in an ice–methanol bath. To this was added 100 g (0.560 mole) of the tetramethoxy butene and 110 ml. of carbon tetrachloride. A solution of 102.5 g. (0.640 mole) of bromine in 50 ml. of carbon tetrachloride was slowly added to the reaction maintaining the temperature between 0° to 10°. Addition took 2 hr. after which an opaque red mixture resulted. This was stirred at room temperature for 1.5 hr. and then the reaction mixture was concentrated by blowing with a nitrogen stream. The mixture was then filtered to give 35 g. of a crystalline product and 171 g. of a liquid. After removing the last traces of solvent from the liquid and treating it with cold petroleum ether (b.p. 40–60°), a precipitate formed to give a total of 145 g. (77%) of crystalline product, m.p. 99°–99.5° (n.m.r. confirmed the structure).

Anal. Calcd. for $C_8H_{16}O_4Br_2$: C, 28.5; H, 4.76; Br, 47.6. Found: C, 28.03; H, 4.55; Br, 47.2.

1,1,4,4-Tetramethoxybutyne-2 (III).—A solution of 18.68 g. (0.166 mole) of potassium *t*-butoxide in 120 ml. of *t*-butyl alcohol was prepared in a 500 ml. two-necked flask in a nitrogen atmosphere drybox. The flask was then stoppered and removed from the drybox. The reaction flask was set in a heating mantle in the hood and fitted with a reflux condenser with a calcium chloride drying tube. The crystalline dibromo compound (29 g., 0.083 mole) was added under a nitrogen blanket, and the reaction slurry was magnetically stirred and heated to reflux. Reflux was continued for 6 hr. and then allowed to cool overnight. The reaction mixture was then filtered. It was necessary to slurry the thick paste with ether in order to filter. The yellow brown filtrate was washed with water and then extracted with ether several times. The combined ether extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated by atmospheric distillation to remove the ether and *t*-butyl alcohol. The final traces of solvent were removed by vacuum distillation. The residue distilled as a colorless liquid at 90–98° (6 mm.). This was redistilled to give 10 g. (70%) of tetramethoxybutyne at 83–86° (6 mm.).

Anal. Calcd. for $C_8H_{14}O_4$: C, 55.17; H, 8.05. Found: C, 54.78; H, 8.11.

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Cleavage of Cyclopropane by *p*-Toluenesulfonyl Chloride and Aluminum Chloride

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The major product of the cleavage of cyclopropane by acyl chlorides and aluminum chloride is not the expected γ-chloro ketone I (by analogy to the action of hydrogen bromide on cyclopropane) but rather the branched β-chloro ketone II.[2]

$$(CH_2)_3 + RCOCl \xrightarrow[CHCl_3]{AlCl_3} \underset{I}{RCO(CH_2)_3Cl} + \underset{II}{RCOCH(CH_3)CH_2Cl} \text{ with II/I} \cong 2$$

We have found that, in contrast to the action of acyl chlorides, *p*-toluenesulfonyl chloride and aluminum chloride cleave cyclopropane to produce 1-chloro-3-(*p*-toluenesulfonyl)propane (III). Although Hart and Levitt[2b] failed to obtain a reaction of sulfonyl chlorides with cyclopropane and aluminum chloride in chloroform, the change of solvents from chloroform to methylene chloride apparently enables the reaction to proceed. Compound III was obtained in 32% conversion

$$(CH_2)_3 + p\text{-}CH_3C_6H_4SO_2Cl \xrightarrow[CH_2Cl_2]{AlCl_3} \underset{III}{p\text{-}CH_3C_6H_4SO_2(CH_2)_3Cl}$$

and was identified by mixture melting point with an authentic sample of sulfone,[3] identical infrared spectra, and identical retention times on the vapor phase chromatogram. The v.p.c. of the reaction mixture indicated the major components to be III and unchanged *p*-toluenesulfonyl chloride. Separation of III from *p*-toluenesulfonyl chloride was effected by column chromatography.

Experimental

Reaction of Cyclopropane with *p*-Toluenesulfonyl Chloride and Aluminum Chloride.—In a 1-l. flask fitted with a stirrer, gas inlet tube, and Dry Ice condenser, were placed 33.3 g. (0.25 mole) of anhydrous aluminum chloride, 450 ml. of dry methylene chloride, and 47.4 g. (0.25 mole) of *p*-toluenesulfonyl chloride. After the solids dissolved, 115 g. (2.74 mole) of cyclopropane was added over a 5-hr. period. The solution was stirred overnight at room temperature (without use of the Dry Ice condenser). The next day 42 g. (1.0 mole) more of cyclopropane was added, and the reaction mixture was again stirred overnight at room temperature. The reaction mixture was poured into 300 g. of water containing 60 ml. of concentrated hydrochloric acid. The methylene chloride was separated and washed with eight equal portions of water. The methylene chloride was dried over anhydrous sodium sulfate, filtered, and the solvent removed under vacuum. The partly-solidified oil was first analyzed by v.p.c. (2 ft. silicon rubber column at 125° in an F and M instrument) using chloroform as the solvent. There were three main peaks corresponding to the solvent, *p*-toluenesulfonyl chloride, and the chlorosulfone III. The retention times corresponded to

(1) National Institutes of Health Predoctoral Fellow, 1962–1963. Supported in part by the National Institutes of Health under grant no. CY-4536.

(2) (a) H. Hart and O. E. Curtis, Jr., *J. Am. Chem. Soc.*, **79**, 931 (1957); (b) H. Hart and G. Levitt, *J. Org. Chem.*, **24**, 1261 (1959); (c) H. Hart and R. A. Martin, *ibid.*, **24**, 1267 (1959).

(3) W. E. Truce and L. Lindy, *ibid.*, **26**, 1463 (1961).