

TABLE II
 LIST OF DERIVATIVES

Compound	Derivative	M.p., °C.	Carbon, %		Hydrogen, %		Nitrogen, %	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
CF ₃ CHOHCH ₂ CO ₂ C ₂ H ₅	Phenylurethan	70.0-70.5					4.58	4.62
C ₃ F ₇ CHOHCH ₂ CO ₂ C ₂ H ₅	Phenylurethan	77.5-78.0	44.44	44.51	3.46	3.52	3.46	3.58
CF ₃ CHOHCH ₂ CO ₂ H	<i>p</i> -Bromophenacyl ester	110.0-111.0	40.28	40.28	2.96	2.96		
C ₃ F ₇ CHOHCH ₂ CO ₂ H	<i>p</i> -Bromophenacyl ester	127.0-127.5	36.92	36.59	2.20	2.33		
CF ₃ CH=CHCO ₂ H	Anilide	125.0-126.0					6.52	6.42
C ₃ F ₇ CH=CHCO ₂ H	Anilide	130.0-131.0					4.44	4.44
C ₃ F ₇ CH ₂ CH ₂ CO ₂ H	Anilide ^a	100.0	45.43	45.34	3.15	3.13	4.42	4.58

^a Also prepared from the ester.

CH₂CH₂CO₂H, m.p. 32.5-33.0°; CF₃CH=CHCO₂H, m.p. 55.5-56.0°; C₃F₇CH₂CH₂CO₂H, m.p. 38.5-39.0°; C₃F₇CH=CHCO₂H, m.p. 48.5-49.0°.

The apparatus was a Beckman Model H-2 pH meter which was standardized before each titration with standard buffer solutions of pH 4.00 and 7.00. Titrations were conducted at 25.00 ± 0.02° in a Sargent constant temperature bath having a mercury thermoregulator.

Two of the acids (CF₃CH₂CH₂CO₂H and CF₃CH=CHCO₂H) were readily soluble in water and a sample of each was easily prepared for titration by dissolving a small amount in approximately 200 ml. of water. The other two were not as soluble and it was necessary to prepare saturated solutions of each by allowing them to stand for 24 hours in one liter of water (contained in an erlenmeyer flask stoppered and protected with an Ascarite filled drying tube) with occasional swirling, then pipetting samples for titration. The water was prepared by passing distilled water through an ion exchange resin and had a pH range of 6.90-7.00.

The acid solution to be titrated was contained in a 400-ml. beaker which was placed in the constant temperature bath at least 20 minutes prior to titration, with a slow stream of nitrogen maintained over its surface to ensure exclusion

of CO₂. Titrations were conducted by adding a measured amount of standard base and mechanically stirring until the pH remained constant.

The ionization constants were calculated from the mid-points of the curves, at which point pH = p*K*, and at other points on the curves by the use of Henderson's equation as described by Glasstone.¹² The results obtained are presented in Table Ia; and in Table Ib these values and those of perfluoroacetic and perfluorobutyric acids are compared with their non-fluorine containing analogs.

Preparation of Derivatives.—These were prepared in the usual manner.^{13,14} Melting points were determined with a Fisher-Johns melting point stage and the values reported are corrected. The derivatives are listed in Table II.

(12) S. Glasstone, "Textbook of Physical Chemistry," 2nd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 1003.

(13) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948.

(14) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1948.

MIDLAND, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Preparation and Properties of Some Compounds Containing the 4,4,4-Trifluorocrotyl Group¹

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The preparation and reactions of several compounds containing the 4,4,4-trifluorocrotyl group are described, and an unusual reaction of lithium aluminum hydride—the reduction of an α,β -dibromoester to an α,β -unsaturated alcohol at *ca.* -80°—is reported.

In a previous paper³ it was reported that the hydrolysis of ethyl 4,4,4-trifluorocrotonate with aqueous base resulted in hydration of the double bond. This gave substance to the belief that the 4,4,4-trifluorocrotonyl group was unusually reactive, and prompted further investigation. The present paper describes some new reactions of ethyl 4,4,4-trifluorocrotonate, and the use of both the ester and 4,4,4-trifluorocrotonic acid in the preparation of other compounds containing the 4,4,4-trifluorocrotonyl group.

The preparation of ethyl 4,4,4-trifluorocrotonate and 4,4,4-trifluorocrotonic acid have been reported previously.⁴ Ethyl 2,3-dibromo-4,4,4-trifluorobu-

tyrate was synthesized by refluxing a solution of bromine, ethyl 4,4,4-trifluorocrotonate and carbon tetrachloride. The reaction of this dibromoester with excess lithium aluminum hydride at *ca.* -80° produced unexpected results. Instead of obtaining the di- or monobrominated alcohol or the saturated alcohol,⁵ 4,4,4-trifluorocrotyl alcohol was obtained in yields of 50%. An alternative synthesis of this alcohol was achieved by the reaction of sodium trimethoxyborohydride with 4,4,4-trifluorocrotonyl chloride. This latter compound was prepared from either 4,4,4-trifluorocrotonic acid or a mixture of this acid and formic acid (obtained as the residue from the acidolysis of ethyl 4,4,4-trifluorocrotonate) and benzoyl chloride, a procedure reported by Brown.⁶ An attempt to prepare this same alcohol by the dehydration of 4,4,4-trifluoro-1,3-butanediol

(1) Part of a paper presented before the Division of Organic Chemistry, 124th National Meeting of the American Chemical Society, Chicago, Illinois, September, 1953.

(2) Abstracted from the doctoral dissertation of D. D. Smith, Purdue University.

(3) E. T. McBee, O. R. Pierce and D. D. Smith, *THIS JOURNAL*, **76**, 3722 (1954).

(4) (a) H. M. Walborsky and M. Schwarz, *ibid.*, **75**, 3241 (1953); (b) R. N. Haszeldine, *J. Chem. Soc.*, 3495 (1952), reported the acid, only; (c) A. L. Henne and C. J. Fox, *THIS JOURNAL*, **76**, 479 (1954).

(5) L. W. Trevoy and W. G. Brown (*THIS JOURNAL*, **71**, 1675 (1949)) obtained styrene from dibromostyrene and lithium aluminum hydride using a reaction medium of refluxing tetrahydrofuran; but under the same conditions they found that ethyl 2,3-dibromo-3-phenylpropionate was reduced to hydrocinnamyl alcohol.

(6) H. C. Brown, *ibid.*, **60**, 1325 (1938).

with phosphorus pentoxide resulted in failure. The diol reacted vigorously with the dehydrating agent, decomposing to hydrogen fluoride and carbonaceous material. Preparation of the diol was accomplished by a lithium aluminum hydride reduction of ethyl 3-hydroxy-4,4,4-trifluorobutyrate. A Bouveault-Blanc⁷ reduction of ethyl 4,4,4-trifluorocrotonate also failed to yield the desired alcohol.

In an endeavor to prepare 4,4,4-trifluorocrotonaldehyde two procedures were employed. The first was a reduction method involving the Rosenmund reaction with the acid chloride. When this was conducted in the usual manner^{8a,b} no aldehyde was obtained. Using benzene as the solvent and palladium-barium sulfate catalyst with Quinoline-S regulator, 84% of the acid chloride was recovered in the form of the acid; and using ether as the solvent with palladium-charcoal catalyst and Quinoline-S regulator, 83% of the acid chloride was recovered unchanged. The alternate method was oxidative and it proved to be successful, although the aldehyde could not be isolated in the pure state, but rather as its 2,4-dinitrophenylhydrazone. The procedure used was a modification of the Oppenauer oxidation⁹ as developed by Lauchenauer and Schinz,¹⁰ and it was applied to 4,4,4-trifluorocrotyl alcohol.

Ethyl trifluoroacetate when reacting with ethyl and isopropyl Grignard reagents is known to produce, in addition to the expected tertiary alcohol, a secondary alcohol as a reduction product.¹¹ In spite of the fact that ethyl 4,4,4-trifluorocrotonate is a vinyllog of that compound, under identical conditions it failed to yield any reduction product. In each instance, the only substance isolated was the 1-4 addition product in yields of 40%. Although the yields were low the assertion may be made that reduction did not occur, because no olefin was obtained from the interaction of the Grignard reagent with the ester—a requirement of reduction.¹¹

Because the reaction of lithium aluminum hydride with an α,β -dibromoester to produce an α,β -unsaturated alcohol has not been reported previously, a rigorous proof of structure of the product herein reported (4,4,4-trifluorocrotyl alcohol) was deemed necessary. That the substance was an alcohol was shown by the formation of a characteristic phenylurethan when it was reacting with phenyl isocyanate. Unsaturation was indicated by the addition of bromine, and reaction with dilute permanganate solution. An infrared spectrum confirmed the presence of the hydroxyl group (a broad peak at $3\ \mu$) and the double bond (a long sharp peak at $5.9\ \mu$). The index of refraction of the alcohol obtained by independent synthesis was identical to that of the alcohol in question, and the infrared spectra of both alcohols were superimposable. Finally, the analytical data were compatible

with those required by calculation for an alcohol having the empirical formula $C_4H_5OF_3$; and the possibility of the dimer was ruled out because of the relatively low boiling point (128°).

The proof of structure of the products isolated from the reaction of ethyl and isopropyl Grignard reagents with ethyl 4,4,4-trifluorocrotonate is not as rigorous, but there is no doubt that the assigned structures (the 1-4 addition products) are correct. These substances reacted in a positive, manner toward a standard test for esters¹² and derivatives characteristic of esters were obtained. These facts, together with other evidence that ethyl 4,4,4-trifluorocrotonate undergoes the normal mode of addition^{3a} (*i.e.*, 1-4 addition), substantiate the structures assigned.

Acknowledgment.—The authors wish to express their appreciation to the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, for their financial support of this work.

Experimental¹³

Ethyl 2,3-Dibromo-4,4,4-trifluorobutyrate.—A 1-liter, 3-necked flask was fitted with a reflux condenser, Hershberg type Tru-bore stirrer and an addition funnel. Ethyl trifluorocrotonate (76 g., 0.45 mole) was dissolved in 150 ml. of carbon tetrachloride contained in the flask and the solution was brought to reflux. Bromine (90 g., 0.56 mole) was added through the addition funnel in a dropwise fashion, and occasionally additional amounts of carbon tetrachloride were added through the condenser to maintain the bromine in solution—in all, 150 ml. more was added. The reaction mixture was refluxed for 24 hours after the bromine addition, illuminating the flask with a 100-watt bulb. The excess bromine and carbon tetrachloride were removed by distillation at atmospheric pressure, and the residue was distilled at reduced pressure, b.p. $65-92^\circ$ (15 mm.), as a preliminary purification measure. This distillate was rectified to obtain 125 g. (0.38 mole, 84.5%) of the dibromoester, b.p. $90.0-92.0^\circ$ (15 mm.), n_D^{20} 1.4448, d_4^{25} 1.823.

Anal. Calcd. for $C_6H_7O_2Br_2F_3$: C, 21.9; Br, 48.8. Found: C, 22.0; Br, 48.8.

4,4,4-Trifluorocrotonyl Chloride (Brown's Procedure⁶).
A. From 4,4,4-Trifluorocrotonic Acid.—A 100-ml., 3-necked flask was equipped with a thermometer well and a glass helices packed column (6 in. \times 10 mm.) fitted with a variable take-off head cooled by means of a water-cooled condenser. The latter was topped by a cold finger condenser cooled by a Dry Ice-trichloroethylene slush, and the exit was vented to a hood. (If the cold finger condenser is omitted much of the product is swept out by hydrogen chloride.) The third neck was used to charge the flask and it was stoppered during the reaction. The receiver was cooled in ice-water and protected with a drying tube filled with calcium chloride.

The flask was charged with benzoyl chloride (60 g., 0.42 mole) and 4,4,4-trifluorocrotonic acid (20 g., 0.14 mole). The solution was slowly heated to 195° , during which time the acid chloride distilled from the reaction mixture (b.p. $64-72^\circ$). This material was rectified through a small jacketed column filled with $1/8$ in. Pyrex glass helices, to obtain 11.5 g. (0.07 mole, 50%) of the acid chloride, b.p. $77.0-77.5^\circ$, n_D^{20} 1.3703, d_4^{25} 1.362; found neut. equiv. 79.9; calcd. 79.3.

Anal. Calcd. for $C_4H_2OClF_3$: C, 30.3; H, 1.26. Found: C, 30.1; H, 1.41.

B. From a Mixture of 4,4,4-Trifluorocrotonic Acid and Formic Acid.—The apparatus was the same as that described previously, except for the flask which was 500 ml. in capacity. Its third neck was equipped with a dropping funnel, the top of which was protected with a drying tube.

(12) N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," T. Y. Crowell Co., New York, N. Y., 1947, p. 121.

(13) Analyses by the Galbraith Microanalytical Laboratories, Knoxville, Tenn.

(7) L. Bouveault and G. Blanc, *Compt. rend.*, **136**, 1676 (1903).
(8) (a) R. Adams, ed., "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 368. (b) D. R. Husted and A. H. Ahlbrecht, *THIS JOURNAL*, **74**, 5422 (1952).
(9) R. Oppenauer, *Rec. trav. chim.*, **56**, 141 (1937).
(10) A. Lauchenauer and H. Schinz, *Helv. Chim. Acta*, **32**, 1265 (1949).
(11) E. T. McBee, O. R. Pierce and J. F. Higgins, *THIS JOURNAL*, **74**, 1736 (1952).

Benzoyl chloride (300 g.) was added to the flask and a solution of 4,4,4-trifluorocrotonic acid (obtained as the residue from the acidolysis of 100 g., 0.60 mole of ethyl 4,4,4-trifluorocrotonate with formic acid after removal of ethyl formate as described previously⁸) was placed in the dropping funnel. The benzoyl chloride was heated to 150–160° and maintained at that temperature while the contents of the dropping funnel were added to it in a dropwise manner, during which time the acid chloride slowly distilled from the flask. When addition was complete another 100 g. of benzoyl chloride was added to the reaction flask and the temperature of its contents was raised to 190–200° until no more acid chloride was obtained.

The crude acid chloride was rectified to obtain 65.0 g. (0.40 mole) of pure material. The over-all yield from the ester was 67%.

4,4,4-Trifluoro-1,3-butanediol.—Lithium aluminum hydride (12.0 g., 0.32 mole) was dissolved in 200 ml. of anhydrous ether contained in a 1-liter, 3-necked flask equipped with a Hershberg type Tru-bore stirrer, reflux condenser and an addition funnel. The solution was chilled, and ethyl 3-hydroxy-4,4,4-trifluorobutyrate (46.5 g., 0.25 mole) dissolved in an equal volume of ether was added to it dropwise over a one-hour period. The reaction mixture was stirred an additional 12 hours during which time it warmed to room temperature, then the excess hydride was destroyed with 95% ethanol and a solution was added which had been made by pouring 50 ml. of concentrated sulfuric acid over 250 g. of ice.

The acid layer was separated and washed twice with 100-ml. portions of ether and then discarded, combining the washings with the organic layer. The ether was removed by distillation, then benzene was added to remove water and ethanol by azeotropic distillation. The residue was distilled, b.p. 104–105° (20 mm.), to obtain a viscous, cloudy liquid which solidified upon standing for several hours at 0°. This solid was white, crystalline and deliquescent in air. The yield was 30 g. (0.21 mole, 83%).

Anal. Calcd. for C₄H₇O₂F₃: C, 33.3; H, 4.87. Found: C, 33.3; H, 4.95.

4,4,4-Trifluorocrotyl Alcohol. A. By the Action of Lithium Aluminum Hydride on Ethyl 2,3-Dibromo-4,4,4-trifluorobutyrate.—A 1-l., 3-necked flask was equipped with a Hershberg type, Tru-bore stirrer, a reflux condenser and a dropping funnel having a pressure-equalizing side arm. The top of the dropping funnel was fitted with a gas inlet tube to permit the reaction to be conducted in a nitrogen atmosphere.

Lithium aluminum hydride (20 g., 0.5 mole) was dissolved in 400 ml. of dry ether contained in the flask and the solution was cooled to ca. –80° in a Dry Ice–trichloroethylene bath. A solution of ethyl 2,3-dibromo-4,4,4-trifluorobutyrate (163 g., 0.50 mole) in 200 ml. of ether was placed in the dropping funnel and added to the cold solution in the reaction flask dropwise, over a two-hour period. Stirring was maintained for an additional 20-hour period (at ca. –80°), then the excess hydride was destroyed with 95% ethanol. The reaction complex was hydrolyzed by pouring it into a solution made by adding 100 ml. of concentrated sulfuric acid to 1 kg. of ice. The organic layer was separated and the acid layer was washed twice with 100-ml. portions of ether. A test for bromide ion in the acid layer was made by bubbling chlorine through a small sample. The formation of a dark brown color soluble in carbon tetrachloride indicated the presence of bromine.

The combined organic layer and ether washings were dried over Drierite, then the ether was removed by distillation. About 25 ml. of benzene was added and distilled to remove the last traces of water and ethanol by azeotropic distillation. (This step is quite important—its omission results in a considerable quantity of azeotropic forerun in the subsequent rectification.) After all the benzene had distilled the residue was distilled at reduced pressure, b.p. 35–54° (28 mm.), for preliminary purification, and the distillate thus obtained was rectified to obtain 33.0 g. (0.25 mole, 50%) of 4,4,4-trifluorocrotyl alcohol, b.p. 128.0–128.5°, *n*_D²⁰ 1.3578, *d*₄²⁵ 1.256.

Anal. Calcd. for C₄H₅OF₃: C, 38.1; H, 3.97. Found: C, 38.2; H, 3.98.

B. By the Action of Sodium Trimethoxyborohydride on 4,4,4-Trifluorocrotonyl Chloride.¹⁴—The apparatus em-

ployed was identical to that described for the lithium aluminum hydride reduction, and a nitrogen atmosphere was maintained throughout the reaction.

The reaction flask was flamed dry in a stream of nitrogen, then charged with 750 ml. of tetrahydrofuran (dried by distillation from lithium aluminum hydride) and sodium hydride (18.0 g., 0.75 mole). The mixture was heated to reflux and methyl borate (73.0 g., 0.70 mole rectified before use) was added to it dropwise. When addition was complete the reaction mixture was refluxed two hours longer, then it was allowed to cool and settle. The solution was filtered under a pressure of nitrogen through a filter stick plugged with glass wool into a dry 1-liter, 3-necked flask, chilled in an ice-water bath and equipped with a Hershberg type, sealed stirrer, a reflux condenser and a dropping funnel having a pressure-equalizing side arm.

A solution of 4,4,4-trifluorocrotonyl chloride (52.0 g., 0.30 mole) in 150 ml. of dry tetrahydrofuran was placed in the dropping funnel and added to the chilled reducing agent in a dropwise fashion. After an additional two hours of stirring, the excess reducing agent was destroyed by the cautious addition of water and the reaction complex was hydrolyzed by pouring it into a solution made by adding 50 ml. of concentrated sulfuric acid to 1 kg. of ice. The resulting homogeneous solution was extracted with ether until the aqueous portion did not diminish in volume with further extraction—about 1500 ml. of ether was required.

The organic layer was dried over anhydrous sodium sulfate, then the tetrahydrofuran and ether were removed by distillation. Rectification of the residue yielded 12.0 g. (0.10 mole, 33%) of 4,4,4-trifluorocrotyl alcohol.

Reaction of Grignard Reagents with Ethyl 4,4,4-Trifluorocrotonate. Procedure.—The Grignard reagent was prepared in the usual manner, using magnesium of high purity, and filtered into a 500-ml., 3-necked flask equipped with a reflux condenser, a sealed stirrer and an addition funnel. A solution of the ester in an equal volume of ether was then added to the Grignard reagent (nitrogen atmosphere), the addition being conducted at ice temperature and requiring one hour to complete. After standing overnight at room temperature the mixture was hydrolyzed by the method indicated, the organic layer was separated and the aqueous layer (or magnesium salts) extracted three times with ether. The combined ether washings and organic layer were dried and the ether was removed by distillation. The residue was then distilled by the method indicated.

A. Isopropylmagnesium Bromide.—The Grignard reagent was prepared from isopropyl bromide (74 g., 0.60 mole) and magnesium turnings (14.4 g., 0.60 mole). During addition of the ester (33.5 g., 0.20 mole) a Dry Ice-cooled trap was connected to the outlet of the condenser, and afterward it was noted that no propylene was formed. The reaction mixture was hydrolyzed with ice-cold, 10% aqueous sulfuric acid, then treated as described.

Rectification produced 17.0 g. (0.08 mole, 40%) of material identified as ethyl 3-(trifluoromethyl)-4-methylpentanoate, b.p. 98.0–99.0° (65 mm.), *n*_D²⁰ 1.3850, *d*₄²⁵ 1.113.

Anal. Calcd. for C₉H₁₅O₂F₃: C, 50.9; H, 7.08. Found: C, 51.3; H, 7.67.

In view of the discrepancy in analyses, both the anilide and hydrazide were prepared and found to confirm the assigned structure (see Table I).

B. Ethylmagnesium Iodide.—The Grignard reagent was prepared from ethyl iodide (93 g., 0.60 mole) and magnesium turnings (14.4 g., 0.60 mole). After addition of the ester (33.5 g., 0.20 mole) the reaction mixture was hydrolyzed with a saturated solution of ammonium chloride. The organic layer and ether washings were combined, and the ether was removed under reduced pressure without further drying. The residue was distilled through a short column packed with 1/8 in. glass helices.

After a short forerun there was obtained 15.9 g. (0.08 mole, 40%) of material identified as ethyl 3-(trifluoromethyl)-pentanoate, b.p. 62.0–65.0° (25 mm.), *n*_D²⁰ 1.3750, *d*₄²⁵ 1.110.

Anal. Calcd. for C₈H₁₃O₂F₃: C, 48.5; H, 6.57. Found: C, 48.7; H, 6.76.

Oppenauer Oxidation of 4,4,4-Trifluorocrotyl Alcohol (Lauchauer and Schinz Modification¹⁰).—A 50-ml., 2-necked flask was equipped with a short jacketed column having a variable take-off head with a water-cooled condenser, and a small addition funnel.

(14) H. C. Brown and E. J. Mead, *THIS JOURNAL*, **75**, 6263 (1953).

TABLE I
 LIST OF DERIVATIVES

Compound	Derivative	M.p., °C.	Element	Calcd., %	Composition Found, %
CF ₃ CH=CHCOCl	N-Methyl amide	110.0	N	9.16	9.07
CF ₃ CHBrCHBrCO ₂ C ₂ H ₅	Benzylamine hydrobromide	220
CF ₃ CH=CHCH ₂ OH	Phenylurethan	63.0	N	5.72	5.71
CH ₃ CH—CHCH ₂ CO ₂ C ₂ H ₅	Hydrazide acid	41.0 ^a	N ^b	14.15	14.29
	anilide	129.0	N	5.41	5.45
CH ₃ CF ₃					
CH ₃ CH ₂ CHCH ₂ CO ₂ C ₂ H ₅	Hydrazide acid	65.0	N	15.2	15.2
	anilide	81.0	N	5.72	5.75
CF ₃					
CF ₃ CH=CHCHO	2,4-Dinitrophenylhydrazone	226.0	C and H N	39.5; 2.30 18.4	39.6; 2.30 18.4

^a Apparently this is the m.p. of a hydrate. After drying in an Abderhalden pistol over phosphorus pentoxide the material turned liquid upon exposure to air, then resolidified to the 41.0° material. ^b Analysis performed on the dried material.

Freshly distilled aluminum isopropoxide (5.5 g., 0.027 mole) was placed in the flask and 4,4,4-trifluorocrotyl alcohol (10 g., 0.08 mole) was added to it in one portion. The pressure in the system was reduced to 100 mm. and the flask was heated slowly to 65–70° by means of an oil-bath. After one hour at this temperature, during which time isopropyl alcohol slowly distilled from the reaction flask, the temperature of the flask was raised to 110° to drive off the last traces of isopropyl alcohol, then the pressure was lowered to 20 mm. whereupon 1.3 g. of 4,4,4-trifluorocrotyl alcohol was recovered.

Anisaldehyde (16.3 g., 0.12 mole) was placed in the addition funnel, the flask was warmed to 65° and the pressure was lowered to 100 mm. The anisaldehyde was added dropwise to the white solid in the reaction flask, which started to darken and finally turned into a black, tarry mass. Upon lowering the pressure further and slowly raising the temperature of the oil-bath a clear, water white distillate

was obtained, b.p. 70–76° (70 mm.). This liquid weighed 3.0 g. and was converted into its 2,4-dinitrophenylhydrazone, m.p. 226° (see Table I for analysis).

Preparation of Derivatives.—These were prepared in the usual manner.^{15,16} Note that benzylamine hydrobromide was obtained (instead of the expected benzyl amide) when benzylamine was added to ethyl 2,3-dibromo-4,4,4-trifluorobutyrate. Such a phenomenon is not unusual.¹⁷ The derivatives are listed in Table I.

(15) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, New York, N. Y., 1948.

(16) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1948.

(17) C. A. Buehler and C. A. Mackenzie, *THIS JOURNAL*, **59**, 421 (1937).

MIDLAND, MICHIGAN

NOTES

A New Synthesis of 1,2-Dialkoxyethanes

BY LEWIS A. GIST, JR., AND CLARENCE T. MASON

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In the course of an investigation involving the behavior of various metals on halogenated ethers, it was observed that chloromethyl alkyl ethers are able to undergo Wurtz coupling in the presence of sodium to give 1,2-dialkoxyethanes. Oda and Teramura¹ state that this reaction with sodium occurs and they report good yields of the 1,2-dialkoxyethanes when metallic copper or iron is used as a condensing agent, but they give no experimental details. Jain, *et al.*,² on the other hand, found that with sodium the 1-chloro-1-alkoxymethanes undergo Wurtz-Fittig coupling with some aromatic compounds having bromine attached to the ring, but not with benzyl bromide, and they report no products which are formed from the condensation of the ether with itself.

(1) R. Oda and K. Teramura, *Bull. Inst. Chem. Res. Kyoto Univ.*, **26**, 88 (1951).

(2) N. C. Jain, R. Kushall and S. Deshapande, *J. Indian Chem. Soc.*, **28**, 49 (1951).

In the present work the reaction of chloromethyl alkyl ethers with sodium is found to proceed in a normal manner except that there is usually a considerable amount of polymerized material left in the reaction flask. It is observed that sodium-toluene dispersions³ seem to give higher yields than sodium shot. No attempt has been made, however, to find optimum conditions for maximum yields.

 TABLE I
 ROCH₂CH₂OR

R	B.p., °C.		n _D ²⁰	d ₄ ²⁰	Yield, %
	°C.	Mm.			
CH ₃	83–85	760	1.3739 ²⁴	0.8602 ³³	27
C ₂ H ₅	120–124	760	1.3886 ²⁵	.8421 ³⁰	32
C ₃ H ₇ ^a	158–165	760	1.3964 ³⁰	.8307 ³⁰	72 ^b
C ₄ H ₉	200–201	760	1.4055 ²⁵	.8351 ²⁸	79 ^b
C ₆ H ₁₁	218–220	755	1.3962 ³²	.8318 ³²	42
<i>i</i> -C ₃ H ₇	42–43	3	1.3945 ³²	.8096 ³²	26
<i>i</i> -C ₃ H ₇	64–67	7	1.3949 ³²	.8189 ³²	42

^a Anal. Calcd. for C₈H₁₈O₂: C, 65.71; H, 12.41. Found: C, 65.73; H, 12.62. ^b Prepared with dispersed sodium.

(3) Furnished through the courtesy of Dr. John Nobis of the National Distillers Products Corp.