hydrochloric acid and boiled gently for twenty minutes. The solid which separated on cooling was filtered and dried. The product weighed 9.5 g. (88%). Recrystallization from 2% formic acid gave small needles exhibiting parallel extinction and decomposing upon heating.

2,4-Diamino-6,7-dimethylpyrimido[4,5-b]pyrazine.—This compound was prepared in 85% yield by warming a mixture of 50 g. of 2,4,5,6-tetraminopyrimidine bisulfite, 20 ml. of biacetyl and 300 ml. of water to approximately 80° for one hour. Recrystallization from 0.1 *N* hydrochloric acid gave small prisms exhibiting parallel extinction and progressively darkening without melting upon heating.

2,4-Diamino-6,7-diphenylpyrimido[4,5-b]pyrazine.—A mixture of 5 g. of benzil, 5 g. of 2,4,5,6-tetraminopyrimidine bisulfite, 3 ml. of concentrated hydrochloric acid, 50 ml. of ethanol, 50 ml. of methyl ethyl ketone and 100 ml. of water was refluxed for two hours. The solid which separated on changing the *p*H to 6 and cooling was recrystallized from 80% formic acid to give small elongated prisms in 84% yield. The crystals exhibited parallel extinction and melted with decomposition at 280–283° (cor.).

Anal. Calcd. for $C_{18}H_{14}N_6$: C, 68.77; N, 26.74. Found: C, 68.89, 69.12; N, 26.74, 26.96.

2,4-Diaminoacenaphtho[1,2-e]pyrimido[4,5-b]pyrazine.—A solution of 1.0 g. of acenaphthenequinone in 25 ml. of dimethylformamide was added to a mixture of 4.5 g. of 2,4,5,6-tetraminopyrimidine bisulfite, 50 ml. of water and 5 ml. of concentrated hydrochloric acid. After heating for four hours on the steam-bath, the mixture was adjusted to *p*H 6 and cooled. The solid obtained in 90% yield was recrystallized from 80% formic acid to give small needles which showed parallel extinction and which progressively darkened without melting upon heating.

2,4-Diaminophenanthro[9,10-e]pyrimido[4,5-b]pyrazine.—A mixture of 2 g. of 2,4,5,6-tetraminopyrimidine bisulfite, 1.5 g. of phenanthrenequinone, 250 ml. of 95% ethanol and 5 ml. of 10% aqueous sodium hydroxide was refluxed for six hours. The solid which separated on cooling was crystallized from 80% formic acid to give an 84% yield of sheaves of small needles exhibiting parallel extinction. Upon heating, the crystals began to sinter at approximately 340° and progessively darkened without melting.

2,4-Diamino-6(or 7)methylpyrimido[4,5-b]pyrazine.—This compound resulted in 90% yield from a mixture of 6 g. of methyl glyoxal, 15 g. of 2,4,5,6-tetraminopyrimidine bisulfite and 200 ml. of boiling water. Recrystallization from 0.1 *N* hydrochloric acid gave prisms showing parallel extinction and darkening without melting upon heating.

Anal. Calcd. for $C_7H_8N_6$: C, 47.72; N, 47.71. Found: C, 47.65, 48.11; N, 47.73, 47.85.

Elementary Analysis of Compounds.—Compounds 3 and 6 of Table I were analyzed for carbon by a modification of the method of Parr.[8] The combustion mixture consisted of 2.5 g. of sodium peroxide, 0.5 g. of potassium perchlorate and 0.2 g. of powdered aluminum for a sample of approximately 50 mg.

The same two compounds were analyzed for nitrogen by the method of Friedrich[9] using a mixture of copper sulfate, potassium sulfate and powdered selenium as catalyst for the digestion.

Summary

2,4-Diaminopyrimido[4,5-b]pyrazine and several of its derivatives have been synthesized. Ultraviolet absorption spectra of solutions of the compounds in dilute acid have been determined.

[8] Parr, This Journal, 29, 1606 (1907).

[9] Pregl-Grant, "Quantitative Organic Microanalysis," The Blakiston Co., Philadelphia, Pa., 1946, p. 82.

Ithaca, N. Y. Received April 8, 1947

[Contribution from the Chemical Laboratories of Stanford University, Northwestern University, and Corn Products Refining Company]

Crystalline 2,3,4,6-Tetrapropionyl-β-D-glucose

By William A. Bonner, Charles D. Hurd and Sidney M. Cantor

A large-scale propionylation of α-D-glucose at 100°, using propionic anhydride and sodium acetate, was performed with the assistance of R. J. Smith and E. A. Cleveland, Jr. On subsequent processing, the volatile materials were removed by steam distillation. A sirupy propionate was obtained which crystallized to the extent of about 5% of the weight of the sirup after standing four months at room temperature. The white crystals, which were isolated by centrifuging and purified by washing with petroleum ether, melted at 111-112°, $[\alpha]^{28}\mathrm{D}$ 21.8° (*c*, 1.42; ethanol). Preliminary work on the characterization of this crystalline product yielded results suggesting 2,3,4,6-tetrapropionyl-β-D-glucose as a probable structure. Accordingly, synthesis of this substance was undertaken.

Sirupy D-glucose pentapropionate was converted into tetrapropionyl-α-D-glucosyl bromide by action of hydrogen bromide in propionic acid. The resulting bromo compound was a strongly dextro-rotatory liquid. Since it decomposed rapidly, it was converted immediately into 2,3,4,6-tetrapropionyl-β-D-glucose. This material was crystalline, identical with the material above. Although several crystalline aryl tetrapropionyl-D-aldohexosides have been reported earlier,[1] all of the previously reported[2] hexose propionates have been sirups. This crystalline propionate is, therefore, unusual.

2,3,4,6-Tetrapropionyl-β-D-glucose shows marked reducing properties and mutarotates in alcohol. It was quantitatively propionylated in pyridine at −10° to give β-D-glucose pentapropionate, a sirup, $[\alpha]^{25}\mathrm{D}$ 14.29°. This latter compound showed no mutarotation in alcohol. Another sirupy pentapropionate was obtained, $[\alpha]^{25}\mathrm{D}$ 64.5°, by propionylating a mutarotated sample of the tetrapropionylglucose at room temperature. From these specific rotations and the

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[1] Oden, *Arkiv. Kemi, Min. Geol.*, 6, 18 (1917); *C. A.*, 12, 581 (1918); Hurd and Bonner, This Journal, 67, 1764 (1945); *J. Org. Chem.*, 10, 603 (1945); 11, 50 (1946).

[2] Hess and Messmer, *Ber.*, 54, 511 (1921); Hurd and Gordon, This Journal, 63, 2657 (1941).

mutarotation of β-D-glucose tetrapropionate described below, it seems apparent that the "α-pentapropionylglucose" ($[\alpha]^{16}\text{D}$ 61.06°) of Hess and Messmer[2] is simply a mixture of the anomeric α- and β-D-glucose pentapropionates near the equilibrium point.

In characterizing our crystalline tetrapropionate further, we have studied its mutarotation at two temperatures, calculated the sum of the rate constants for the mutarotation, and compared these data with the corresponding data for 2,3,4,6-tetraacetyl-β-D-glucose.

At 23° in ethanol the crystalline 2,3,4,6-tetrapropionyl-β-D-glucose mutarotates from 2.9° to an equilibrium value of 74.7°. The reaction

$$\alpha\text{-form} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \beta\text{-form}$$

was studied by means of Lowry's equation.[3] The sum of the rate constants, $k_1 + k_2$, is calculated as 0.00124 ± 0.00014 min.$^{-1}$. At 34° in methanol the tetrapropionate mutarotates from 12.3 to 69.6°, and $k_1 + k_2$ has the value 0.00465 ± 0.00031 min.$^{-1}$. Fischer and Delbrück[4] have studied the mutarotation of 2,3,4,6-tetraacetyl-β-D-glucose in ethanol at 22° and found a rise from 2.2° to 82.7°. We have calculated $k_1 + k_2$ for this mutarotation from their data and find the value to be 0.00127 ± 0.00016 min.$^{-1}$. Thus, $k_1 + k_2$ at about 23° is almost identical for the tetrapropionate and tetraacetate, indicating that the nature of the acyl group has little effect on the rate of mutarotation. Curves for these mutarotations are given in Fig. 1.

2,3,4,6-Tetraacetyl-α-D-glucose has been prepared[5] and found to mutarotate from 139.4 to 83.1°, an equilibrium value in excellent agreement with that noted for the β-anomer. In conjunction with the value for $k_1 + k_2$ calculated above, the equation[6]

$$K_{\text{equil.}} = \frac{k_1}{k_2} = \frac{\alpha_\alpha - \alpha_\infty}{\alpha_\infty - \alpha_\beta}$$

permits the individual rate constants for the mutarotations of the 2,3,4,6-tetraacetylglucoses to be determined. The value for k_1 is 0.000521 min.$^{-1}$, and k_2 is 0.000744 min.$^{-1}$. Although optically pure 2,3,4,6-tetrapropionyl-α-D-glucose is not known and the above calculations cannot be made, it is probable that the individual rate constants for the mutarotations of the tetrapropionates are of the same order of magnitude as those calculated for the tetraacetates, since the mutarotation curves are quite similar. Such considerations also suggest the probability that the specific rotations of pure 2,3,4,6-tetrapropionyl-α-D-glucose and of α-D-glucose pentapropionate lie rather close to those of the acetyl analogs.

It is interesting to note that the sum of the mutarotation constants ($k_1 + k_2$) for D-glucose at 25° in 95% ethanol[7] is 0.00052 min.$^{-1}$, a figure considerably lower than the values for either the tetraacetate (0.00127) or the tetrapropionate (0.00124). Although the normal ring structures of glucose are the pyranose and furanose forms, presumably all of the alcoholic hydroxyl groups in the glucose molecule contribute to the strength of the cyclic structures prevailing in a particular environment. Since an acyclic modification is probably the rate controlling factor in mutarotation,[8] it would follow that substitution of the hydroxyl groups by acyl groups weakens this ring structure, allowing more of the acyclic intermediate to be formed, thereby increasing the rate of mutarotation.

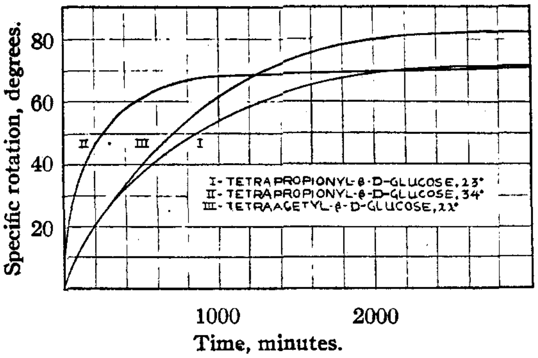

Fig. 1.—Mutarotations of tetraacyl-β-D-glucoses.

Experimental

Tetrapropionyl-α-D-glucosyl Bromide.—The method used for the preparation of this compound was analogous to that of Ohle and co-workers[9] for the synthesis of tetraacetyl-α-D-galactosyl bromide. D-Glucose pentapropionate (23 g.) was dissolved in a solution (55 g.) of 31% hydrogen bromide in propionic acid, and the mixture was permitted to stand at room temperature for forty hours. It was then poured into ice-water, ether-extracted, the ether solution twice washed with water, then with saturated sodium bicarbonate solution until gas evolution ceased, then again with water. It was dried over magnesium sulfate, and decolorized completely by two filtrations through Norit and Celite. The solvent was removed at 50–60° *in vacuo* to give 19 g. (81%) of a thin straw colored sirup with a pungent odor. The rotation, analysis and following reaction were undertaken immediately, as the compound decomposed very rapidly on standing. Darkening began instantly, and on standing overnight the substance had become a thick tar smelling strongly of hydrogen bromide and propionic acid. The specific rotation of the freshly prepared substance was $[\alpha]^{25}\text{D}$ 116° (*c*, 2.213; chloroform). Analysis in a Parr bomb gave 20.5% Br, in contrast to the theoretical, 17.1%. The error is probably due to the inability to purify the sirup once it is obtained, and to its rapid decomposition. In a second experiment, using 40 g. of D-glucose pentapropionate and 100 g. of 31% hydrogen bromide in propionic acid, 34.5 g. (85%) of crude product was isolated having a higher specific rotation, $[\alpha]^{25}\text{D}$ 141° (*c*, 1.230; chloroform). This preparation also gave a high bromine analysis.

2,3,4,6-Tetrapropionyl-β-D-glucose.—The above bromide (34.1 g.) from the second experiment was immedi-

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[3] Lowry, *J. Chem. Soc.*, **75**, 211 (1899).

[4] Fischer and Delbrück, *Ber.*, **42**, 2778 (1909).

[5] Schlubach and Wolf, *ibid.*, **62**, 1507 (1929).

[6] "Polarimetry, Saccharimetry and the Sugars," Circ. C440, Nat. Bur. Standards, 1942, p. 447.

[7] Rowley, THIS JOURNAL, **62**, 2563 (1940).

[8] Cantor and Peniston, *ibid.*, **62**, 2113 (1940).

[9] Ohle, Maracek and Bourjau, *Ber.*, **62**, 848 (1929).

ately dissolved in acetone (50 ml.), and water (1.5 ml.) was added. The solution was cooled in ice. Silver carbonate (23 g.) was added, and the mixture was stirred at 0° for one hour. Carbon dioxide was evolved vigorously at the outset of the reaction. The silver salts were removed by filtration and washed with acetone. The halogen-free acetone solution was concentrated rapidly to dryness *in vacuo* at 60°. The residue was dissolved in dry ether, and decolorized by filtration through Norit and Celite, then concentrated to dryness. There was obtained a quantitative yield (30 g.) of crude, amber sirup which crystallized spontaneously. The substance was recrystallized by dissolving in a minimum of alcohol, adding Skellysolve A until turbid, and alternately shaking and blowing air over the two-phase mixture. A second crop was obtained by repeating the operation on the mother liquors. A third crop resulted on placing the final mother liquors at −15° for two days. The combined crops weighed 16.3 g. (55.3%) and melted at 105.5–107°. Recrystallization, using the same technique, raised the m. p. to 108.5–110°: $[\alpha]^{25}_D$ 21.2° (*c*, 0.485; chloroform).

Anal. Calcd. for $C_{18}H_{28}O_{10}$: C, 53.46; H, 6.99. Found[10]: C, 53.60; H, 7.12. Propionyl: Calcd. for $C_6H_8O_6(OCC_2H_5)_4$: 56.5. Found[11]: 57.5, 57.4.

The substance is readily soluble in most organic solvents, but practically insoluble in water. It distills unchanged at mercury-vapor pump pressures under approximately the same conditions as does glucose pentapropionate.[2] The distillate is a clear, amber sirup which crystallizes unseeded on standing several minutes. The material reduces hot Fehling solution, as does the sirupy pentapropionate. In contrast to the behavior of the latter, however, it shows a rapid reducing action on Tollens reagent.

Mutarotation Data.—In Table I are presented data for the mutarotation of 2,3,4,6-tetrapropionyl-β-D-glucose at 23° and 34° and for the mutarotation of 2,3,4,6-tetraacetyl-β-D-glucose[4] at 22°. The sum of the rate constants for the mutarotations, $k_1 + k_2$, as calculated from the equation[8]

$$k_1 + k_2 = \frac{2.303}{t} \log \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}$$

are given in the last column.

TABLE I

MUTAROTATIONS OF 2,3,5,6-TETRAACYL-β-D-GLUCOSES

Acyl	Solvent	Temp., °C.	Concn., g./100 ml.	α(°)	$[\alpha]_D$	Time, min.	$k_1 + k_2$ min.$^{-1}$
Propionyl	EtOH	23	1.380	0.04	2.9	3	.....
				.32	23.2	236	0.00141
				.48	34.8	471	.00125
				.88	63.8	1416	.00133
				.98	71.0	3120	.00096
				1.03	74.7	∞	.....
							Av. 0.00124 ± 0.00014
Propionyl	MeOH	34	1.218[a]	0.30	12.3	5	.....
				.63	25.9	50	0.00532
				.76	31.2	85	.00469
				.94	38.5	120	.00510
				1.04	42.7	155	.00485
				1.15	47.2	200	.00467
				1.26	51.6	260	.00445
				1.35	55.4	320	.00434
				1.42	58.2	380	.00424
				1.46	59.8	425	.00415
				1.70	69.6	1420	.....
							Av. 0.00465 ± 0.00031
Acetyl	EtOH	22	4.552	0.10	2.2	10	.....
				.20	4.4	30	0.00091
				.36	7.9	60	.00123
				2.66	58.4	900	.00130
				3.04	66.6	1200	.00135
				3.33	73.0	1380	.00154
				3.77	82.7		.....
							Av. 0.00127 ± 0.00012

Polarimeter tube length in this run was 2 dm.; in the other runs it was 1 dm.

Conversion of 2,3,4,6-Tetrapropionyl-β-D-glucose into β-D-Glucose Pentaacetate.—2,3,4,6-Tetrapropionyl-β-D-glucose (1.00 g.) was dissolved in methanol (150 ml.) and a small chip of sodium was added. After ninety minutes, the solvent was removed *in vacuo*. The residue was heated with acetic anhydride (15 ml.) and sodium acetate (1.3 g.) for two hours at 100°. The mixture was cooled, poured into water, permitted to stand for several hours, then extracted with ether. The ether solution was washed with water, sodium bicarbonate solution, again with water, dried over sodium sulfate, and decolorized by filtration through Norit and Celite. After removal of the solvent, there resulted 0.68 g. (70%) of residue. This was crystallized from 2-propanol to give β-D-glucose pentaacetate, m. p. 130.5–131.5°.

When the acetylation of the depropionylated residue was carried out with acetic anhydride in pyridine, the crystalline product obtained was a mixture of the anomeric α- and β-glucose pentaacetates, as indicated by its low, diffuse melting point (110–116°) and the failure of the melting point to be raised appreciably by a second recrystallization.

Conversion of 2,3,4,6-Tetrapropionyl-β-D-glucose to β-D-Glucose Pentapropionate.—2,3,4,6-Tetrapropionyl-β-D-glucose (1.00 g.) was dissolved in pyridine (15 ml.) and cooled to −10°, then treated with propionic anhydride (4 ml.) of the same temperature. The mixture stood at −10° for four days, then at room temperature for fifteen hours. It was then poured into water (50 ml.), allowed to stand for three hours, extracted into ether, and the product isolated in the usual manner[12] after washing with dilute hydrochloric acid and sodium bicarbonate solution. The yield of sirupy β-D-glucose pentapropionate was quantitative. The rotation was $[\alpha]^{25}_D$ 14.29° (*c*, 3.955; chloroform). No mutarotation in methanol was observed. The sirup was analyzed without further purification.

Anal. Calcd. for $C_{21}H_{32}O_{11}$: C, 54.85; H, 7.00. Found: C, 54.28; H, 6.57.

Conversion of Mutarotated 2,3,4,6-Tetrapropionyl-D-glucose into D-Glucose Pentapropionate.—2,3,4,6-Tetrapropionyl-β-D-glucose (0.14 g.) was dissolved in 95% ethanol (10 ml.) and allowed to mutarotate to its equilibrium value at room temperature. The alcohol was distilled *in vacuo* leaving a sirup which began to crystallize slowly. This was dissolved in pyridine (3 ml.) and propionic anhydride (2 ml.). Excess of anhydride was destroyed after twenty-one hours (25°) by adding 20 g. of water. After standing for three hours with occasional shaking, the mixture was extracted twice with ether. The ether solution was washed,[12] dried over sodium sulfate, filtered and the solvent distilled at 100° (last traces *in vacuo*). There remained 0.13 g. (82%) of sirupy, equilibrized D-glucose pentapropionate: $[\alpha]^{24}_D$ 64.5° (*c*, 4.265; chloroform).

Tetrapropionyl-α-D-glucosyl Chloride.—Sirupy D-glucose pentapropionate (12 g.) was dissolved in dry chloroform (50 ml.), and treated with a solution of titanium tetrachloride (6 ml.) in dry chloroform (25 ml.) after the manner of Pacsu.[13] The mixture was protected from moisture and refluxed for six hours, then cooled and poured into water. The chloroform layer was separated and washed several times with water. Serious difficulty was encountered with emulsions during the washing. Each time the layers were separated as well as possible, and in the final washing the emulsion was completely broken down by suction filtration through Celite. The chloroform solution was dried over sodium sulfate, partially decolorized by filtration through Norit and Celite,

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(10) Analysis by Dr. T. S. Ma.

(11) Analysis by the method of Kunz and Hudson, THIS JOURNAL, **48**, 1978 (1926).

(12) Hurd, Englis, Bonner and Rogers, *ibid.*, **66**, 2015 (1944).

(13) Pacsu, *Ber.*, **61**, 1508 (1928).

and the solvent removed *in vacuo* at 35°. The dark, sirupy residue was dissolved in ether (150 ml.) and decolorization completed by filtration again through Norit and Celite. Removal of the ether left 6.1 g. (55%) of clear, amber sirup having a high, positive rotation, $[\alpha]^{25}_{\text{D}}$ 130.6° (*c*, 6.530; chloroform). This compound was unstable on standing, but did not decompose as rapidly as the corresponding bromide.

Anal. Calcd. for $C_{18}H_{27}O_9Cl$: Cl, 8.41. Found[14]: Cl, 8.66.

Summary

Crystalline 2,3,4,6-tetrapropionyl-β-D-glucose has been prepared by controlled hydrolysis of tetrapropionyl-α-D-glucosyl bromide. The crystalline nature is striking, since D-glucose pentapropionate and others are sirups.

The mutarotation of 2,3,4,6-tetrapropionyl-β-D-glucose has been studied at two temperatures, the sum of the rate constants for these mutarotations calculated, and these data compared with the corresponding values for 2,3,4,6-tetraacetyl-β-D-glucose.

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RECEIVED APRIL 9, 1947

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[14] Analyzed by the procedure of Vaughn and Nieuwland, *Ind. Eng. Chem., Anal. Ed.*, **3**, 294 (1931).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

The Alkaline Condensation of Fluorinated Esters with Esters and Ketones[1]

BY ALBERT L. HENNE, MELVIN S. NEWMAN, LAURENCE L. QUILL AND ROBERT A. STANIFORTH

A series of alkaline condensations have been performed, linking a fluorinated ester with another ester, a ketone or a fluorinated ketone. At that time (1942–1943) the only known condensation of this kind was the preparation of a trifluoroacetoacetate, $CF_3COCH_2CO_2R$, by Swarts,[1a] who also obtained trifluoroacetone, CF_3COCH_3, from it by decomposition with 10% sulfuric acid; recently a similar work has been reported.[2]

First, Swarts' work was repeated, using an improved technique. Next, ethyl difluoroacetate was successfully condensed with ethyl acetate to yield the difluoroacetoacetate. In contrast it was not found possible to condense a trifluoro- with a difluoroacetate, nor was it found possible to condense a difluoroacetate with itself. With ketones, two condensations were tried, which both succeeded well: a trifluoroacetate and acetone yielded trifluoroacetylacetone, $CF_3COCH_2COCH_3$, while a trifluoroacetate and trifluoroacetone yielded hexafluoroacetylacetone, $CF_3COCH_2COCF_3$.

In all cases, the condensed compounds gave stable chelated derivatives with such ease, that it became advantageous to separate the condensates from the reaction mixtures as their crystalline copper derivatives. These chelated derivatives were easily recrystallized from paraffin hydrocarbons or from alcohol; they proved more stable, lower melting and more volatile than their unfluorinated analogs. A number of metal derivatives were prepared which will be reported separately.[3]

Experimental

Preparation of Fluorinated Esters.—Trifluoroacetic and difluoroacetic acids were obtained by oxidation of a propene derivative.[4] They were esterified either by treatment of their sodium salt with ethyl sulfate, or by heating their salt in an excess of alcohol with a small amount of sulfuric acid, distilling the azeotropic mixture of ester and alcohol as formed, and ultimately washing off the alcohol by means of calcium chloride. It was noted that an appreciable amount of ether was formed when trifluoroacetic acid reacted with ethanol or with butanol but that the amount of ether formed in the case of difluoroacetic acid was small. This is well in line with the known strength of these acids. Properties observed were: $CF_3CO_2C_2H_5$: b. p. 60.5°, n_{D} 1.3093 at 15° and $CHF_2CO_2C_2H_5$: b. p. 99°, n_{D} 1.3463 at 20°. The yield of pure ester was 75 to 80% and additional impure fractions were obtained which accounted for all of the material used.

Condensation and Isolation Procedures.—All condensations were performed in ether, with sodium ethylate freshly prepared by treating one equivalent of absolute ethanol with one equivalent of finely dispersed sodium. To the resulting suspension was added one equivalent of dry fluorinated ester, whereupon solution took place with a slight evolution of heat. The second compound (ester or ketone) was then added, and the mixture refluxed for about fifty hours, a period of time which may be unnecessarily long. On account of the avidity of the condensates for water, the following procedure of isolation was adopted. The reaction mixture was treated with a concentrated solution of sodium bisulfate in very slight excess over neutralization requirements, then with a clear aqueous solution of cupric acetate. The organic layer was distilled off, then the crystalline copper derivative was filtered and recrystallized from a suitable solvent. The dry copper derivative was suspended in dry ether, in which it partly dissolved, and was subjected to a stream of hydrogen sulfide. After removal of the cupric sulfide, the condensed compound was separated from the ether by fractional distillation, with rigorous precautions to avoid losses by volatility.

$CF_3COCH_2CO_2Et$, b. p. 131.8°; over-all yield 54%; copper chelate as green crystals from alcohol, m. p. 189°, Cu % 33.4 found, 33.5 calcd.

CF_3COCH_3, b. p. 21°, 75% yield by refluxing the preceding compound for two hours with 10% sulfuric acid, collecting the vapors on phosphoric anhydride to destroy the hydrate, and distilling therefrom; 2,4-dinitrophenylhydrazone, m. p. 139°, N % 19.06 found, 18.98 calcd.

$CHF_2COCH_2CO_2Et$, b. p. 72° at 30 mm., n_{D} 1.4018 at 20°, 35% over-all yield. F % found 22.3, calcd. 22.9; copper chelate as blue crystalline prisms m. p. 183–184°. Low yield attributed to faulty technique.

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[1] This paper is based on work performed under Contract W-7405-eng-95 for the Manhattan Project and the information therein will appear in Division VII of the Manhattan Project Technical Series, as part of the contribution of the Department of Chemistry, Ohio State University.

[1a] Swarts, *Bull. class sci. Acad. roy. Belg.*, [5] **12**, 692 (1926).

[2] Breslow and co-workers, THIS JOURNAL, **68**, 100 (1946).

[3] Quill and Staniforth, private communication.

[4] Henne, Alderson and Newman, THIS JOURNAL, **67**, 918–919 (1945); Henne, U. S. Patent 2,371,757, March 20, 1945.