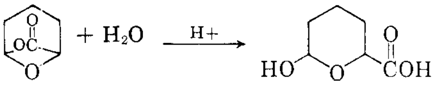
fied (with excess mineral acid) and the unsaturated acid (III) had been removed by extraction. This same hydroxy acid was prepared in essentially quantitative yield by the acid-catalyzed hydration of 7-oxo-6,8-dioxabicyclo[3.2.1]octane.



EXPERIMENTAL[8]

7-Oxo-6,8-dioxabicyclo[3.2.1]octane and 1,4-dimethyl-7-oxo-6,8-dioxabicyclo[3.2.1]octane. These materials were prepared *via* the silver-catalyzed oxidation with molecular oxygen of acrolein dimer and methacrolein dimer, respectively. The oxidation has been reported elsewhere,[6] and involves the oxidation of the aldehydes with molecular oxygen with a silver catalyst in an aqueous solution of sodium hydroxide. The products of the oxidation are the salts of the acids from which the lactones are recovered by acidification, extraction, and distillation.

Esterification procedure. For the preparation of the "symmetrical" acetal-esters, the lactone and alcohol were used in the quantities shown in Table I. These materials along with the sulfuric acid catalyst (0.5 to 0.75 weight %) were charged to the kettle of a distillation assembly which carried a liquid-liquid separating head. Sufficient isopropyl ether was added (200–400 ml.) to insure ready separation of the water of reaction during the reflux period. At the completion of the water removal, the mixtures were allowed to stand at room temperature for several hours, usually overnight. The sulfuric acid was neutralized with sodium ethoxide or sodium acetate and the mixtures distilled to recover the alkyl 6-alkoxytetrahydropyran-2-carboxylates.

Transesterification procedure. The transesterifications shown in Table II were conducted in a standard manner using sodium methoxide or sodium ethoxide as a catalyst. The acetal-ester and alcohol were mixed in the proportions shown in Table II and 0.5% catalyst (sodium methoxide or sodium ethoxide) by weight of the reactants was added. The mixtures were distilled to remove most of the lower boiling, exchanged alcohol at atmospheric pressure. The last traces of the exchanged alcohols were removed under reduced pressure followed by removal of the excess reactant alcohol and the product ester. For the last reactant combination shown in Table II, the mixture containing the catalyst was permitted to stand 16 hr. at room temperature. The coproduct allyl alcohol was then removed by distillation at essentially room temperature under reduced pressure. Inasmuch as distinctly superior results were obtained for this experiment as compared to the other reactant combinations, this may be the preferred method of performing this transesterification.

Poly(3,4-dihydro-2H-pyran-2-carboxylic acid). Four hundred g. of aqueous solution containing 100 g. of sodium 3,4-dihydro-2H-pyran-2-carboxylate which was neutral to phenolphthalein, was acidified with 26.2 g. of concentrated sulfuric acid (80% of theory) in 130 ml. of water. The acidification was conducted at 0° and in the presence of 300 ml. of ethyl ether. The aqueous layer was removed and extracted twice with 200 ml. of ether. The combined extracts were distilled (steam bath) under reduced pressure to remove the ether. The residue amounted to 59 g. and was a colorless, viscous liquid which was water-soluble and evolved carbon dioxide upon treatment with aqueous sodium bicarbonate. Immediate titration with standard base to a phenolphthalein end point gave a purity of approximately 50.5% as the monomeric acid. The value was somewhat uncertain due to the fading end point. Determination of the purity by bromination (0°) gave an approximate value of 45% purity. The infrared spectrum contained discrete absorption bands at 3.7, 5.7, 7.7, and 10.6μ characteristic of the carboxyl group and at 6.04μ characteristic of the unsaturation. In a few hours the material had resinified to a nonpourable state and was tacky.

Anal. Calcd. for $C_6H_8O_3$: C, 56.20; H, 6.29; Sap. Equiv., 128.1. Found: C, 56.70; H, 6.17; Sap. Equiv. 135.

After the polymer had stood for approximately 2 months, 31.8 g. was heated (oil bath at 160 to 200°) under 3 mm. of pressure. The vapors were passed through a gooseneck and condensed to provide 24 g. of a water-insoluble liquid. This material was identified as the lactone, 7-oxo-6,8-dioxabicyclo[3.2.1]octane, on the basis of its boiling point (65°/3 mm.; lit.[3] value is 63/3 mm.) and refractive index (n_D^{20} 1.4582; lit.[3] value is n_D^{20} 1.4587).

6-Hydroxytetrahydropyran-2-carboxylic acid. An aqueous solution of 430 ml. remaining from the acidification with excess sulfuric acid of the sodium 3,4-dihydro-2H-pyran-2-carboxylate and extraction with isopropyl ether was evaporated to dryness at room temperature. On the basis of the acid balance, the aqueous solution could have contained a maximum of 30 g. of the 6-hydroxytetrahydropyran-2-carboxylic acid. The light colored, tacky solid was extracted several times with ethyl ether and the extracts evaporated. The white solid was recrystallized from ethyl acetate to provide 2.5 g. of white prisms or needles believed to be 6-hydroxytetrahydropyran-2-carboxylic acid and which melted at 89.5–90.5°.

This same acid was prepared as follows: a suspension of 25.6 g. (0.2 mol.) of 7-oxo-6,8-dioxabicyclo[3.2.1]octane, 20 ml. of water, and 7.3 ml. of $0.5N$ sulfuric acid was shaken at room temperature. After several minutes the solution temperature increased to about 40° accompanied by a complete solution of the organic phase. The solution was neutralized with 7.3 ml. of $0.5N$ sodium hydroxide and the water evaporated below 30° using a vacuum desiccator to provide 29.2 g. of 6-hydroxytetrahydropyran-2-carboxylic acid of m.p. 89.0–90.5°. A melting point of 89.0–90.5° was observed for a mixture of the acids isolated from the two sources. The infrared spectrum contained no absorption for ethylenic unsaturation but did contain strong bands characteristic of the —OH and —COOH groups.

Anal. Calcd. for $C_6H_{10}O_4$: C, 49.3; H, 7.0; Neut. Equiv. 146. Found: C, 49.0; H, 7.0; Neut. Equiv., 147.

Acknowledgment. We wish to thank Mr. J. Bodenschatz for the elemental analyses reported. We also thank Mr. W. H. Rankin and Mr. C. C. Caldwell for their assistance with portions of the experimental work.

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[8] All melting points are corrected, boiling points are uncorrected.

The Preparation of Certain Amino-Substituted Perfluoroalkyl-s-Triazines

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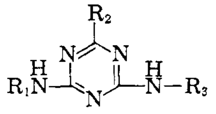
As part of a study of cellulose-reactive materials, the preparation of a number of amino-substituted perfluoroalkyl-s-triazines was undertaken. It is known that the *N*-methylol derivatives of 2-alkyl-4,6-diamino-s-triazines can be used as crosslinking

TABLE I

PERFLUOROALKYL-*s*-TRIAZINES



R_1	R_2	R_3	M.P. °C.	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N	Yield
H	CF_3	H	318–321[a]	26.8	2.25	39.1	26.9	2.23	38.8	90
H	CF_3CF_2	H	255–256	26.2	1.76	30.5	26.2	1.75	30.7	73
H	$CF_3(CF_2)_6$	H	177–179	25.0	0.80	14.6	25.0	1.37	14.7	80
C_6H_5[b]	CF_3	H	185–186	47.1	3.16	27.4	47.2	3.15	27.5	81
p-ClC_6H_5[b,c]	CF_3	*p*-ClC_6H_5	182–185	49.2[d]	3.75	14.5	49.1	3.55	14.3	20
H	—(CF_2)—$_3$	H	>320	29.2	2.18		28.8	2.50		68

[a] Sublimed. [b] For each mole biguanide, 2 moles of methyl trifluoroacetate and 1 mole sodium methoxide used. [c] Reactants shaken in autoclave for 24 hours at 100° before drowning in H_2O. [d] Product recrystallized from dioxane and retained 1 mole of dioxane of crystallization, $C_{16}H_{10}Cl_2F_3N_5 \cdot C_2H_4O_2$; Calcd. Cl, 14.5; Found: Cl, 14.6.

agents for cotton. It was, therefore, of interest to determine the effect of replacing the hydrogen atoms attached to the alkyl group with fluorine. The only compound of this type reported in the literature, 6-amino-4-anilino-2-trifluoromethyl-*s*-triazine, was prepared by Overberger, Michelotti and Carabateas.[1]

In preparing the *s*-triazine derivatives, the general method reported by Thurston and Kaiser[2] of reacting biguanides with esters was followed. The reaction of unsubstituted biguanide with methyl esters of various perfluorocarboxylic acids was extremely clear-cut, and good yields of pure materials were obtained. In contrast, the reaction of monosubstituted biguanides with methyl trifluoroacetate required not only longer times, but also, in some cases, the presence of sodium methoxide. The reaction of a disubstituted biguanide with methyl trifluoroacetate required even more vigorous conditions: cyclization of 1,5-bis-(*p*-chlorophenyl)biguanide to the corresponding *s*-triazine derivative necessitated heating the reactants in methanol in an autoclave at 100° in the presence of sodium methoxide for 24 hr.

EXPERIMENTAL[3]

Materials. Methyl trifluoroacetate,[4] methyl pentafluoropropionate,[5] methyl heptafluorobutyrate,[6] methyl pentadecafluorocaprylate,[6] and dimethyl hexafluoroglutarate,[7] were all prepared by methods given in the literature.

n-Butylbiguanide hydrochloride. A mixture of 27.3 g. (0.25 mole) of butylamine hydrochloride and 21.0 g. (0.25 mole) of cyanoguanidine was stirred on the steam bath until fusion occurred and then at 130 ± 5° for 4.5 hr.

The cooled melt was taken up in boiling acetone and allowed to reflux for 1 hr. and upon cooling, there separated 16.6 g. (34.6%) of white crystals, m.p. 152–164°. Recrystallization from benzene ethanol raised the m.p. to 176–177.

Anal. Calcd. for $C_6H_{15}N_5 \cdot HCl$: C, 37.2; H, 7.82; N, 36.2. Found: C, 37.3; H, 8.19; N, 36.2.

1,5-Bis-p-chlorophenylbiguanide hydrochloride. The method we report is simpler and less time consuming than that given in the literature.[8] To a stirred slurry of 63. 0g. (0.49 mole) of *p*-chloroaniline, 44.5 g. (0.50 mole) of sodium dicyanamide and 500 ml. of water at 90° was added dropwise over a period of .5 hr., 100 ml. of 4.9*M* HCl. The gray precipitate which formed was chilled and filtered after first adjusting the pH to 3 with conc. HCl. The crude *p*-chlorophenyldicyandiamide, I, after drying at 60° for 24 hr., weighed 80.8 g. (83.5%), m.p. 204–207, and was used in the next step without further purification. A stirred slurry of 30.0 g. (0.15 mole) of I, 21.0 g. (0.16 mole) of *p*-chloroaniline, 50 ml. of Cellosolve, and 250 ml. water was treated dropwise at 97° ± 3 with 25 ml. of 6.6*M* HCl over a 20-minute period. After completion of the addition of the acid, the solution was refluxed for 1.5 hr. and the precipitate collected after cooling and adjusting the pH to 3; 40.8 g. (74%) m.p. 251–253, lit.,[8] 250°.

4,6-Diamino-2-heptafluorobutyl-s-triazine. The preparation of this compound was typical of the *N*-unsubstituted diaminoperfluoroalkyl-*s*-triazines listed in Table I. To a solution of 26.2 g. (0.26 mole) of biguanide and 100 ml. of absolute methanol at 35° was added portion-wise with stirring 68.4 g. (0.3 mole) of methyl heptafluorobutyrate. The temperature of the reaction rose rapidly to the boil, and the rate of addition was such as to maintain a gentle boil. Within a few minutes after all the fluoroester had been added, a heavy white precipitate formed. The reaction mixture was cooled to room temperature and allowed to stir overnight before chilling, filtering and air drying. There was obtained 45.7 g. of a white solid, m.p. 202–204°; concentration of the mother liquor yielded an additional 9.0 g., total yield 75.6%. After recrystallizing from methanol, the product melted 203–204°.

Anal. Calcd. for $C_6H_4F_7N_5$: C, 25.8; H, 1.44; N, 25.1. Found: C, 26.0; H, 1.64; N, 25.2.

6-Amino-4-n-butylamino-2-trifluoromethyl-s-triazine. The preparation of this compound is typical of the *N*-substituted

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[2] J. T. Thurston and D. W. Kaiser, U.S. Patent **2,535,968**.

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diaminoperfluoroalkyl-*s*-triazines listed in Table I, unless otherwise noted. A mixture of 3.86 g. (0.02 mole) of *n*-butylbiguanide hydrochloride, 1.18 g. (0.02 mole) of sodium methoxide, 2.76 g. (0.022 mole) of methyl trifluoroacetate, and 75 ml. of methanol was stirred at room temperature for 4 days, and then drowned in an excess of water. The white crystalline solid which formed from the initial oil weighed 2.75 g. (58.5%) and melted 98–100 .

Anal. Calcd. for $C_8H_{12}F_3N_5$: C, 40.9; H, 5.14; N, 29.8. Found: C, 41.1; H, 5.19; N, 29.6.

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Reduction of Allylic Halides by Lithium Aluminum Hydride[1]

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The lithium aluminum hydride reduction of an allylic halide to the corresponding hydrocarbon has been used as a means of identification and characterization of allylic halides, especially geometrical isomers.[3] There is retention of configuration and no allylic rearrangement with this reaction when the allylic halogen atom is terminal. It has been noted, however, that 2,3,3-trichloro-1-butene gives *trans*-2,3-dichloro-2-butene[4] and 3,4-dibromo-1-butene gives *trans*-2-butene.[5] DeWolf and Young have suggested that this reaction goes by an S_N2' mechanism[6] and the conformational implications of this mechanism have been discussed by Hatch, Gardner and Gilbert.[5] This reaction has now been extended to include 3,4-dichloro-1-butene and two secondary-mono-allylic halides (3-chloro-1-butene and 3-bromo-1-butene).

The reduction of 3,4-dichloro-1-butene by lithium aluminum hydride in tetrahydrofuran gave the expected *trans*-2-butene as indicated by gas-liquid partition chromatography. 3-Chloro-1-butene was prepared along with its allylic isomer, *trans*-1-chloro-2-butene, by the addition of hydrogen chloride to butadiene using concentrated hydrochloric acid.[7] Lithium aluminum hydride reduction of this chloride produced a mixture of hydrocarbons containing *cis*-2-butene (5%), butadiene (8%), *trans*-2-butene (18%) and 1-butene (69%). A similar mixture was obtained from 3-bromo-1-butene. The 3-bromo-1-butene was prepared by allylic rearrangement of *trans*-1-bromo-2-butene.

From these data it would appear that the prediction that secondary allylic halides react by an S_N2' mechanism[5] must be modified. The present indications are that at least one other halogen atom is required to be in the vicinity of the secondary allylic halogen to cause the reaction to go exclusively by this mechanism. The other halogen atom or atoms are also required for the reaction to be stereospecific.[5] The butadiene was formed by dehydrohalogenation caused by the lithium aluminum hydride.

Both *trans*-1-chloro-2-butene (crotyl chloride) and *trans*-1-bromo-2-butene (crotyl bromide) give *trans*-2-butene on reduction with lithium aluminum hydride. 1,4-Dichloro-2-butene prepared by the addition of chlorine to butadiene also gave the expected *trans*-2-butene[8] but a purchased sample of 1,4-dichloro-2-butene formed a mixture of products containing 71% *cis*-2-butene and 29% *trans*-2-butene. This dichloride apparently was produced from 1,4-butyndiol by catalytic hydrogenation followed by conversion of the diol to the corresponding dichloride.

EXPERIMENTAL

3,4-Dichloro-1-butene. This dichloride was purchased from Columbia Organic Chemicals, Inc., Columbia, S.C., and purified by distillation: b.p. 42° (40 mm.); n_D^{25} 1.4615. Lit.[9] b.p. 123° (766 mm.); n_D^{20} 1.4630.

1,4-Dichloro-2-butene. A sample of 1,4-dichloro-2-butene was purchased from Columbia Organic Chemicals, Inc., and distilled: b.p. 72.5° (39 mm.); n_D^{25} 1.4872.[8] *cis* isomer b.p. 152.5° (758 mm.), n_D^{25} 1.4887; *trans* isomer b.p. 155.5° (758 mm.), n_D^{25} 1.4871. *trans*-1,4-dichloro-2-butene was synthesized along with 3,4-dichloro-1-butene by the addition of chlorine (45 g., 0.64 mole) to butadiene (31 g., 0.58 mole) in 200 ml. of chloroform at ice bath temperature. The 1,4-dichloro-2-butene was separated from its isomer by distillation: b.p. 74° (40 mm.); n_D^{25} 1.4863.

3-Chloro-1-butene and 1-chloro-2-butene. A mixture of 3-chloro-1-butene and *trans*-1-chloro-2-butene (crotyl chloride) was obtained by the treatment of butadiene (54 g., 1.00 mole) with an excess of 37% hydrochloric acid saturated with hydrogen chloride.[7] The reaction was carried out in a sealed tube at 25° for 36 hr. The organic layer was washed with a dilute sodium bicarbonate solution, dried and distilled. 3-Chloro-1-butene: b.p. 64° (760 mm.); n_D^{27} 1.4111. Lit.[7] b.p. 63.7° (748 mm.); n_D^{20} 1.4151.

trans-1-Chloro-2-butene: b.p. 84° (760 mm.); n_D^{27} 1.4292. Lit.[7] b.p. 84.8° (752 mm.); n_D^{25} 1.4327.

3-Bromo-1-butene. 3-Bromo-1-butene was obtained as a mixture with *trans*-1-bromo-2-butene by permitting the

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(1) Presented in part at the 136th meeting of the American Chemical Society, Atlantic City, September 13–18, 1959.

(2) Present address: The Dow Chemical Company, Freeport, Texas.

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