Attempt to dehydrogenate VII. A solution of 0.0001 mole each of VII and tetrachloroquinone in 10 ml. of xylene was refluxed 24 hr., allowed to stand at room temperature 48 hr., and worked up by chromatography on an alumina-filled column. Elution with petroleum ether, petroleum ether–benzene, benzene, and benzene-alcohol gave no fraction corresponding to the structure (VIII); unchanged VII was recovered in the second fraction.

Trans-2,3-di-tert-butylsuccinic anhydride (IX) from VI. A suspension of 1.0 g. of VI in an excess of 3% potassium permanganate made basic with 5% potassium hydroxide was stirred overnight. Destruction of the excess permanganate with formic acid and acidification with sulfuric acid gave a precipitate which was filtered off, washed, and dried. The resulting 0.5 g. (53%) of the succinic anhydride IX melted at 112–114°, or 114–115° after sublimation. The melting point was not depressed upon admixture with the product obtained by the permanganate oxidation of I,[3] and the two samples gave identical infrared spectra.

This compound was subjected to titration with sodium aminoethoxide in ethylene diamine: 0.0376 g. of IX required 0.57 ml. of 0.315*N* base. Calcd. for $C_{12}H_{20}O_3$: mol. wt. 212.28. Found: Neut. equiv. 209.4.[13]

Lithium aluminum hydride reduction of I (formation of X). Four g. of I was treated with an excess of lithium aluminum hydride in anhydrous ether over a period of about 2 hr. The excess hydride was destroyed carefully with water, the solution acidified, separated, and the ether evaporated to give 1.8 g. (45%) of white crystals. This material was sublimed at 150° and 4-mm. pressure to give 1.7 g. of X, m.p. 178–179°. It gave a positive enol test with both ferric chloride and copper acetate, and was sufficiently acidic to dissolve in 5% aqueous sodium bicarbonate.

Anal. Calcd. for $C_{14}H_{24}O_3$: C, 69.96; H, 10.07; neut. equiv. 240.33. Found: C, 70.13; H, 9.84; neut. equiv. 242.

Acknowledgment. The writers wish to thank Dr. D. Y. Curtin of the University of Illinois for assistance in interpreting infrared spectra and for his helpful criticism of the manuscript.

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[13] Succinic anhydride itself under the same conditions gave the following: 0.1022 g. of succinic anhydride required 3.33 ml. of 0.315*N* base. Calcd. for $C_4H_4O_3$: mol. wt. 100.07. Found: Neut. equiv. 97.4. We are indebted to Mr. J. M. Harris for these determinations.

[CONTRIBUTION FROM UNIVERSITY OF CALIFORNIA, LAWRENCE RADIATION LABORATORY]

Fluorine-Containing Nitrogen Compounds. I. Trifluoroethylamines

EUGENE R. BISSELL AND MILTON FINGER

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The complete series of methyltrifluoroethylamines having one trifluoroethyl group and 0, 1, 2, or 3 methyl groups has been synthesized. Physical data are reported, and a number of derivatives suitable for characterization have been prepared.

As a part of a study of the properties of fluorine containing nitrogen compounds, we have synthesized and characterized the complete series of methyltrifluoroethylamines containing one trifluoroethyl group and 0, 1, 2, or 3 methyl groups.

2, 2, 2-Trifluoroethylamine, the first member in the series, was first prepared in 1943 by Gilman and Jones[2] by the catalytic hydrogenation of trifluoroacetonitrile. It is also formed in low yield by the Hofmann degradation of β,β,β-trifluoropropionamide or by the Schmidt-Curtius rearrangement of β,β,β-trifluoropropionic acid azide.[3] A United States patent[4] has been issued covering trifluoroethylamine and its production by ammonolysis of trifluoroethyl halides. A more convenient synthesis involving lithium aluminum hydride reduction of trifluoroacetamide was later reported by Bourne, Henry, Tatlow, and Tatlow[5] and by McKay and Vavasour.[6] The process has been patented in Great Britain by the Minnesota Mining and Manufacturing Co.[7]

Some of the higher homologs of methyl-2,2,2-trifluoroethylamine have been prepared by the reduction of carbamates[8] or isocyanates,[9] but methyl-2,2,2-trifluoroethylamine itself, the second member in the series, has not been reported. No tertiary amines or quaternary ammonium salts containing trifluoroethyl groups appear to have been reported.

We have applied the lithium aluminum hydride reduction method to *N*-methyltrifluoroacetamide and to *N*,*N*-dimethyltrifluoroacetamide and obtained methyl-2,2,2-trifluoroethylamine and dimethyl-2,2,2-trifluoroethylamine. Both the amides and the amines were previously unknown. The reduction proceeds with greater vigor and the yields decrease as the degree of substitution of the nitrogen atom increases. With the tertiary amide the reaction is too violent to be controlled easily.

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[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

[2] H. Gilman and R. G. Jones, *J. Am. Chem. Soc.*, **65**, 1458 (1943).

[3] A. L. Henne and J. J. Stewart, *J. Am. Chem. Soc.*, **77**, 1901 (1955).

[4] A. F. Benning and J. D. Park, U. S. Patent **2,348,321** (1944).

[5] E. J. Bourne, S. H. Henry, C. E. M. Tatlow, and J. C. Tatlow, *J. Chem. Soc.*, **4014** (1952).

[6] A. F. McKay and G. R. Vavasour, *Can. J. Chem.*, **32**, 639 (1954).

[7] British Patent **689,425** (1953).

[8] R. L. Dannley and R. G. Taborsky, *J. Org. Chem.*, **22**, 77 (1957).

[9] R. L. Dannley, R. G. Taborsky, and M. Lukin, *J. Org. Chem.*, **21**, 1318 (1956).

TABLE I

REDUCTION OF TRIFLUOROACETAMIDES

Amide	Moles	Hydride	Moles	T°[a]	Time[b]	% Yield
CF_3CONH_2	0.1	$LiAlH_4$	0.2	0	30	57.4[c]
CF_3CONH_2	0.2	$LiAlH_4$	0.4	0	180	52.7[d]
CF_3CONH_2	0.1	$1:1NaBH_4–BF_3\cdot Et_2O$	0.11		60	44.2[d]
$CF_3CONHCH_3$	0.1	$LiAlH_4$	0.2	0	120	55.1[c]
$CF_3CONHCH_3$	0.2	$LiAlH_4$	0.4	−10	120	61.5[c]
$CF_3CONHCH_3$	0.1	$1:1NaBH_4–BF_3\cdot Et_2O$	0.11		30	53.2[d]
$CF_3CON(CH_3)_2$	0.1	$LiAlH_4$	0.2	0	180	11.0[c,e]
$CF_3CON(CH_3)_2$	0.2	$LiAlH_4$	0.4	−78	120	32.1[c,e]
$CF_3CON(CH_3)_2$	0.1	$NaBH_4–AlCl_3$	0.1[f]		60	47.9[d]
$CF_3CON(CH_3)_2$	0.1	$NaBH_4–AlCl_3$	0.1[g]		30	27.5[d]
$CF_3CON(CH_3)_2$	0.1	$NaBH_4–AlCl_3$	0.2[h]		60	16.4[d]
$CF_3CON(CH_3)_2$	0.1	$NaBH_4–AlCl_3$	0.1[i]	0	60	63.9[d]
$CF_3CON(CH_3)_2$	0.1	$1:1NaBH_4–BF_3\cdot Et_2O$	0.11		15	64.7[d]
$CF_3CON(CH_3)_2$	0.1	$1:1NaBH_4–BG\cdot Et_2O$	0.055		10	31.1[d]
$CF_3CON(CH_3)_2$	0.1	$2:1NaBH_4–BF_3\cdot Et_2O$	0.11		30	54.2[d]

[a] Temp. at which addition was made. [b] Time for the addition in minutes. [c] As hydrochloride. [d] As free amine. [e] Contaminated with $(CH_3)_2NH\cdot HCl$. [f] $AlCl_3$ was added as a suspension in 50 ml. of diethylene glycol dimethyl ether. [g] 0.3*M* solution in diethylene glycol dimethyl ether. [i] 0.05 mole of solid $AlCl_3$.

TABLE II

PHYSICAL CONSTANTS

Compound	*d/t* °	n_D^{25}	*p*K	*A*	*B*	*nbp*
$CF_3CH_2NH_2$	1.245/25[a]	1.295[b] (30°)	5.7[b]	7.937	1568	37°
$CF_3CH_2NHCH_3$	1.105/21.5	1.31535	6.05	8.175	1694	47°
$CF_3CH_2N(CH_3)_2$	1.027/24	1.31891	4.75	8.106	1671	47°
$CF_3CH_2N(CH_3)_3OH$			12.43			

[a] Ref. 2. [b] Ref. 3.

Sodium borohydride alone proved to be ineffective in reduction of even the tertiary amide. However, in combination with aluminum chloride or boron trifluoride etherate it proved to be the reagent of choice, at least for the tertiary case. Aluminum chloride presented some problems of its own. When diethylene glycol dimethyl ether solutions were employed, the yields were not satisfactory and the large volume of solvents required were troublesome to remove. Best results were obtained by adding the aluminum chloride as a solid, but the large amounts of heat evolved required extreme caution. Boron trifluoride etherate was simpler to handle and produced comparable results. Freshly distilled etherate was necessary for high yields. Sodium borohydride–boron trifluoride etherate was also a satisfactory reducing agent for trifluoroacetamide and *N*-methyltrifluoroacetamide though the yields were not quite so high as those from lithium aluminum hydride reductions. Table I presents some comparisons of the three reducing agents with the three trifluoroacetamides.

The fourth member in the series, 2,2,2-trifluoroethyltrimethylammonium hydroxide, was obtained as an aqueous solution by treating a solution of the corresponding bromide or iodide with silver oxide. The bromide or iodide could be readily prepared by treatment of dimethyltrifluoroethylamine with methyl bromide or methyl iodide at room temperature. The reaction of 2,2,2-trifluoroethyl iodide with trimethylamine is very sluggish (about 5% in 12 days at room temperature).

Trifluoroethylamine and the two methyltrifluoroethylamines are volatile, colorless, mobile liquids with typical amine like odors. They are miscible with water and with most organic solvents. The electron withdrawing effect of the trifluoromethyl group on base strength is readily apparent from the pK's listed in Table II. The effect of the trifluoromethyl group is just slightly less than that found by Soloway and Lipschitz[10] for the cyano group. Table II also lists the constants A and B for the vapor pressure equation $\log_{10} P = A - B/T$ (P in mm. of Hg. and T in °Kelvin) together with densities, indexes of refraction, and normal boiling points.

The trifluoroethylamines form the usual types of amine derivatives, a number of which are listed in Table III. In view of the anomalous behavior of trifluoroethylamine on treatment with nitrous acid,[11] it was of interest to investigate the action of this reagent on methyltrifluoroethylamine. In the case of the methyl amine the action was normal, leading to the nitrosamine in good yield. The nitrosamine, however, was oxidized to the nitramine only with difficulty; and the nitramine, while colorless when freshly distilled, rapidly turned

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[10] S. Soloway and A. Lipschitz, *J. Org. Chem.*, **23**, 613 (1958).

[11] Anomalous to the extent that the diazo compound is stable; see ref. 2.

TABLE III

Compound	M.P.	Solvent	Calculated % C	Calculated % H	Calculated % N	Found % C	Found % H	Found % N
2,2,2-Trifluoroethylamine								
hydrochloride[a]	>200 subl.	[b]						
hydrobromide	>200 subl.	[b]	13.35	2.80	7.78	13.54	3.28	7.40
p-toluenesulfonate	144–145	[c]	42.68	3.98	5.53	43.08	4.17	5.02
phenylurea	173.5–174	[b]	49.54	4.16	12.84	49.82	4.14	12.60
ethylurethane	48–9		35.09	4.71		34.66	4.57	
Methyl-2,2,2-trifluoroethylamine								
hydrochloride	>200 subl.	[b]	24.09	4.72	9.37	24.07	4.46	8.89
hydrobromide	200–201	[d]	18.57	3.64	7.22	18.86	3.77	7.02
nitrate	135–136	[d]	20.46	4.01	15.91	20.72	3.98	15.61
p-toluenesulfonate	86–87	[e]	44.94	4.53	5.66	45.14	4.55	5.36
phenylurea	146–147	[f]	51.72	4.77	12.06	51.98	4.99	11.84
Dimethyl-2,2,2-trifluoroethylamine								
hydrochloride	160 subl.	[d]	29.37	5.55		29.17	5.94	
hydrobromide	183.5–184	[b]	23.09	4.36	6.73	22.95	4.88	6.56
nitrate	69.8–70.2	[g]	25.27	4.77		25.30	5.08	
2,2,2-Trifluoroethyltrimethylammonium								
bromide	220.5–221	[f]	27.04	4.99		27.15	5.41	
iodide	189–190	[b]	22.32	4.12	5.21	22.68	4.44	4.72

[a] Ref. 5. [b] Ethanol. [c] Benzene. [d] Ethanol-ether. [e] Benzene–petroleum ether. [f] Aqueous ethanol. [g] Isopropanol-ether.

yellow on standing. Anhydrous peroxytrifluoroacetic acid[12] was required for complete oxidation.

EXPERIMENTAL[13]

Amides. Ethyl trifluoroacetate (100 ml., 117 g., 0.82 mole) was saturated at 0° with gaseous ammonia, methylamine, or dimethylamine. After storing at ambient temperatures for about 20 hr. the clear, colorless solution was distilled to yield an ethanol forerun followed by the amide.

Trifluoroacetamide. Yield, 83%; b.p. 159–160°; m.p. 68–70° (lit.[2] 75°).

N-Methyltrifluoroacetamide. Yield, 92%; bp. 156–157°; m.p. 50–51°; x-ray determination of the crystal structure showed it to be monoclinic with a = 7.30 Å, b = 7.61 Å, c = 5.12 Å, and α = 81°. The calculated density was 1.50 g./cc. The analytical sample was recrystallized from ether–petroleum ether and resublimed.

Anal. Calcd. for $C_3H_4F_3NO$: C, 28.35; H, 3.17; N, 11.03. Found: C, 28.60; H, 3.33; N, 11.10.

N,N-Dimethyltrifluoroacetamide. Yield, 87%; b.p. 132–134°; $n_D^{25.2}$ 1.36110, d_{21} 1.232.

Anal. Calcd. for $C_4H_6F_3NO$: C, 34.05; H, 4.29. Found: C, 33.65; H, 4.24.

$LiAlH_4$ Reductions. Under an argon atmosphere, a solution of amide in Na-dried ether (50 ml./0.1 mole) was added at the temp. and in the time specified in Table I to a stirred suspension of $LiAlH_4$ in Na-dried ether (50 ml./0.1 mole). After the addition was complete, the reaction mixture was stirred at the specified temp. for an additional hr. and then stored at room temp. for 16–20 hr. It was then cooled to 0° and decomposed by cautious addition of water (50 ml./0.1 mole of hydride). After stirring for 1 hr. at room temp. the volatile portion of the reaction mixture was distilled off, dried over anhyd. Na_2SO_4, filtered, and saturated with $HCl_{(g)}$. Filtration and drying yielded the amine hydrochloride.

$NaBH_4$ Reductions. In a 500-ml. three necked, round bottomed flask equipped with a stirrer, dropping funnel, and reflux condenser, were placed in the order mentioned 3.8 g. (0.1 mole) of $NaBH_4$, 100 ml. of Na–dried diethylene glycol dimethyl ether, and 0.1 mole of amide. Stirring was started and $AlCl_3$ or freshly distilled BF_3,Et_2O was added over the period specified in Table I. Although some gas was liberated together with considerable heat, unless otherwise specified in Table I, no external cooling was used. The reaction mixture was then stirred at 100° for 1 hr., cooled to room temperature, and decomposed by addition of 50 ml. of 6N HCl. The reaction mixture was then evaporated to dryness at about 1 mm. pressure from a warm water bath. The flask containing the dried residue was fitted with a dropping funnel connected to a vacuum manifold through a −196° trap and evacuated to about 1μ pressure. Saturated aqueous NaOH (50 ml.) was then added from the dropping funnel, and the volatile material was transferred to the trap. The amine was freed from the bulk of the water by passing it twice through traps cooled in an ethylene dichloride slush bath. The remainder of the water was removed from trifluoroethylamine and from methyltrifluoroethylamine by drying over drierite. Ammonia and methylamine were removed by passage through a trap cooled in Dry Ice acetone. With dimethyltrifluoroethylamine both the last of the water and any dimethylamine present could be readily removed by passing the vapors through a small bed of 5A Molecular Sieve.[14]

2,2,2-Trifluoroethylamines. The free amines were obtained either directly from the $NaBH_4$ reduction mixtures or by treatment of the hydrochloride with NaOH[2]. The physical properties are reported in Table II. The infrared spectra taken in the vapor phase show the following bands: for *2,2,2-trifluoroethylamine:* 2.78 (w), 3.22 (m), 6.07 (m), 7.25 (m), 7.9 (s), 8.5 (s), 9.1 (s), 11.40 (m), 11.88 (s), and 13.1 (s) μ; for *methyl-2,2,2-trifluoroethylamine:* 2.71 (w), 3.30 (m), 3.41 (sh), 3.50 (sh), 6.74 (m), 6.82 (m), 7.20 (m), 7.85 (s), 8.20 (s), 8.6 (s), 9.15 (s), 10.35 (m), 12.10 (m), 13.5 (m), and 14.8 (m) μ; for *dimethyl-2,2,2-trifluoroethylamine:* 3.33 (m), 3.57 (m), 6.82 (m), 7.10 (m), 7.59 (s), 7.80 (s), 8.73 (s), 8.98 (s), 9.40 (m), 10.60 (w), 11.90 (w), and 14.9 (w)μ.

Amine derivatives. Hydrochlorides and hydrobromides were prepared by saturating an ethereal solution of the free amine with $HCl_{(g)}$ or $HBr_{(g)}$, centrifuging, drying, and recrystallizing. Nitrates were prepared from the corresponding hydrochlorides by metathesis with $AgNO_3$ in aqueous solution. The p-toluenesulfonates and phenylureas were prepared according to Shriner and Fuson[15] methods 18B and

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(12) W. O. Emmons, *J. Am. Chem. Soc.*, **76**, 3468 (1954).

(13) Melting points are corrected; boiling points are uncorrected.

(14) Linde Air Products Co., 30 East 42nd St., New York 17, N. Y.

(15) R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds*, John Wiley and Sons, Inc., New York, N. Y., 1948, pages 177 and 179.

20, respectively. *N*-2,2,2-Trifluoroethyl ethyl urethane was prepared by treating at room temp. an ethereal solution of the amine with $^1/_2$ equivalent of ethyl chlorocarbonate. The amine hydrochloride was removed by filtration and the urethane recovered by evaporation of the solvent and sublimed.

2,2,2-Trifluoroethyltrimethylammonium bromide. Equimolar amounts of methyl bromide and dimethyltrifluoroethylamine were measured gasometrically and condensed by means of liquid nitrogen into an evacuated tube. The tube was then stored at ambient temps. for several hours. Reaction was essentially quantitative and appeared to occur entirely in the liquid phase.

2,2,2-Trifluoroethyltrimethylammonium iodide. A from dimethyltrifluoroethylamine. The reaction was carried out in the same manner with methyl iodide as with methyl bromide. Solutions of the quaternary iodide were found to liberate iodine quite readily on contact with the air. *B from trifluoroethyl iodide.* Trifluoroethyl iodide[16] (2.10 g., 0.01 mole) and 1095 ml. at 24.5° and 407 mm. (0.24 mole) of trimethylamine were sealed in an evacuated, heavy walled, Pyrex tube of about 9 ml. capacity and stored at ambient temp. for 12 days. The tube was then opened and its volatile contents pumped off. Approximately 120 mg. of solid residue remained.

Methyl-2,2,2-trifluoroethylnitrosamine. To a solution of 37.5 g. (0.25 mole) of methyltrifluoroethylamine hydrochloride in 140 ml. of 10% HCl was added with stirring a solution of 17.5 g. (0.25 mole) of 95% $NaNO_2$ in 75 ml. of water. The temp. was kept below 10° by external cooling during the addition and for an additional hour thereafter. The oily lower layer was separated, and the aqueous phase was extracted 5 times with 25 ml. portions of CH_2Cl_2. After drying over anhyd. Na_2SO_4 the clear yellow solution was distilled to yield, after a CH_2Cl_2 forerun, 26.5 g. (74.5%) of bright yellow nitrosamine, b.p. 131–133°, $d_{22.5}$ 1.287, n_D^{25} 1.36714. Its infrared spectrum shows bands at 6.78, 7.46, 7.93, 8.55, 9.07, 9.64, 12.01, and 13.27μ.

Methyl-2,2,2-trifluoroethylnitramine. The nitrosamine was oxidized by the method of Emmons, Procedure A[13], in 43% yield. The nitramine is a colorless liquid boiling at 76–78°/33 mm., d_{22} 1.400, n_D^{25} 1.38893. Its infrared spectrum shows bands at 6.43, 6.87, 7.14, 7.42, 7.65, 7.92, 8.13, 8.57, 9.11, 9.75, 12.05, 13.07, and 14.22μ.

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LIVERMORE, CALIF.

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[16] Columbia Organic Chemicals Co., Inc., 912 Drake St., Columbia, S. C.

[CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA]

Organic Deuterium Compounds. II. Some Deuterated Tetrahydrofurans[1]

EUGENE R. BISSELL AND MILTON FINGER

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The synthesis and some of the physical properties of tetrahydrofuran-2,2,5,5-d_4, tetrahydrofuran-3,3,4,4-d_4, tetrahydrofuran-2,3,4,5-d_4 and tetrahydrofuran-d_8 are reported. The vapor pressure of tetrahydrofuran was also measured.

As part of a continuing program on the preparation and properties of deuterated organic compounds, we have prepared and measured some of the physical properties of tetrahydrofuran-2,2,5,5-d_4, tetrahydrofuran-3,3,4,4-d_4, tetrahydrofuran-2,3,4,5-d_4 and tetrahydrofuran-d_8. Since comparison data for some of the physical properties reported of tetrahydrofuran itself were not available, they were also measured.

Tetrahydrofuran-2,2,5,5-d_4 was prepared by lithium aluminum deuteride reduction of diethyl succinate followed by cyclization in the presence of phosphoric acid.[2] In preliminary experiments with undeuterated materials it was found unnecessary and even impractical to purify the intermediate 1,4-butanediol because of its viscosity and high boiling point. Some dehydration of the intermediate glycol to allyl alcohol was also observed during the cyclization. In a like manner tetrahydrofuran-3,3,4,4-d_4 and tetrahydrofuran-d_8 were prepared from dimethyl succinate-d_4[3] by reduction with lithium aluminum hydride and lithium aluminum deuteride, respectively, followed by cyclization. Preparation of tetrahydrofuran-3,3,4,4-d_4 by reduction of 1,4-butynediol with deuterium gas, at 4 to 5 atmospheres in the presence of platinum, followed by phosphoric acid cyclization, resulted in material containing only about 48% of the β-hydrogen atoms replaced by deuteriums.

Tetrahydrofuran-2,3,4,5-d_4 was prepared by catalytic reduction (5% rhodium on alumina) of furan in an atmosphere of deuterium. Of the series of compounds prepared this is the only one which can exhibit stereoisomerism. Although the physical properties presented here cannot be used to distinguish which isomer or isomers may be present, the method of preparation renders some of them more probable than others. Catalytic hydrogenation is generally accepted to add hydrogens in pairs *cis* to one another.[4,5] With a diene system

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[1] This work was done under the auspices of the U. S. Atomic Energy Commission.

[2] W. Reppe, U. S. Patent **2,251,292,** August 5, 1941.

[3] A. McLean and R. Adams, *J. Am. Chem. Soc.*, **58,** 804 (1936).

[4] A. Farkas and L. Farkas, *Trans. Faraday Soc.*, **33,** 837 (1937).