sium selenocyanate reacted. The benzene solutions, after concentration under reduced pressure, at 40°, gave a red thick matter, which solidified after two hours, and showed a melting range from 70 to 115°. It consisted of a mixture of selenenyl bromide and selenenyl selenocyanate; after two recrystallizations from hot carbon tetrachloride, small yellow plates of the melting range 81.0–83.8° and with the selenium content of 42.21% were obtained. This melting range, after two more recrystallizations from the same solvent, remained the same, but the selenium content of the substance was raised to 44.33%, and after three more recrystallizations, to 44.46% (calcd. 44.99%).

On account of the low reactivity of this selenenyl bromide at room temperature, an attempt was made, at higher temperature, to increase the yield of the reaction: by heating under reflux, for twelve hours, a mixture of 6.5 g. (0.02 mole) of the bromide in 45 cc. of dry benzene with 3.6 g. (0.025 mole) of potassium selenocyanate and a small amount of "Drierite," under protection against light and humidity of the air, no separation of selenium was noted. After evaporation of the solvent from the filtered solution *in vacuo*, a red thick matter remained, which solidified after several hours. This material, showing a melting range of 70–116°, was again a mixture of the selenenyl bromide and selenenyl selenocyanate, from which, after three recrystallizations from carbon tetrachloride, by heating to 45° and cooling to 0°, yellow plates which melted at 82–84° were isolated. Repeated recrystallizations did not alter this melting range.

Anal. Calcd. for $C_7H_3O_4N_3Se_2$: Se, 44.99; N, 11.97. Found: Se, 44.69; N, 12.04.

At about 150° the substance separates selenium and gives 2,4-dinitrophenyl selenocyanate, which melts at 163°. By heating the substance in glacial acetic acid for some time, at about 120°, selenium is separated, with formation of the aryl selenocyanate. Even in petroleum ether or carbon tetrachloride, heated for long time, the substance separated selenium.

The substance is easily soluble in ether, carbon disulfide, benzene, toluene and xylene, slightly soluble in carbon tetrachloride, acetone, acetic ester, methanol, ethanol and petroleum ether. By heating with methanol or ethanol it separates selenium and gives the diselenide. Alcoholic potassium hydroxide dissolves it with a brownish-red color.

VI. **Reaction of 4-Nitrobenzeneselenyl Bromide with Potassium Selenocyanate.**—This selenenyl bromide (m. p. 91.5–92.5°, from petroleum ether)[5] reacts slowly with potassium selenocyanate, at room temperature; thus, the reaction is incomplete. At a higher temperature, the reaction is not practicable, because the selenenyl selenocyanate or the mixture formed in the reaction is very sensitive against the usual solvents and, for the same reason, the formed selenenyl selenocyanate cannot be isolated from this complex mixture. A typical example of various experiments is the following: 28.0 g. (0.1 mole) of *p*-nitrobenzeneselenenyl bromide, dissolved in 125 cc. of dry benzene, was shaken, in the usual manner, with 16.0 g. (0.11 mole) of potassium selenocyanate for twenty hours. The benzene solution was then filtered, under protection against humidity of the air, from the solid residue (A), which was washed with dry benzene. From the benzene solutions, after evaporation of the solvent at cold, *in vacuo*, a lachrymatory oil resulted, which solidified completely after an hour (B). This matter (30 g.) had a melting range from 88 to 136°, with separation of selenium a little under 136°. From the cooled and solidified material, by extraction with a little hot carbon tetrachloride, *p*-nitrophenyl selenocyanate (m. p. 135–136°) was isolated.

The reddish solid residue (A), carefully dried (15.2 g.), gave 7.0 g. of unaltered potassium selenocyanate by extraction with a little cold acetone; thus, only 9 g. or 62.7% of the theoretical amount reacted. It contained also the equivalent quantity of potassium bromide and red selenium (0.8 g.). The reaction product (B) was thus a mixture of selenenyl bromide, selenenyl selenocyanate and aryl selenocyanate, according to the selenium content (41.23%) which is between that of the selenenyl selenocyanate (51.60%) and that of the aryl selenocyanate (34.77%). The mixture product (B), exposed to air, rapidly separates selenium, and loses also its lachrymatory odor. It dissolves in methanolic potassium hydroxide with a deep red color. By heating in dry carbon tetrachloride, the mixture separates selenium; a brownish-yellow matter, which crystallized by cooling the filtered solution, was a mixture of yellow plates and red selenium; by repeating this treatment, pure *p*-nitrophenyl selenocyanate (m. p. 135–136°; Se, 34.61, calcd., 34.77) was isolated. The same result was obtained by dissolving the mixture in ethyl acetate or by precipitating its solution in benzene or carbon disulfide, by addition of petroleum ether.

The reaction of benzeneselenenyl bromide with potassium selenocyanate in benzene gave a similar unseparable mixture product.

Summary

The preparation of some members of the new class of aromatic selenenyl selenocyanates, ArSeSeCN, and the chemical behavior of these compounds are described.

SÃO PAULO, BRAZIL RECEIVED MAY 31, 1949

[CONTRIBUTION FROM THE NORTHERN REGIONAL RESEARCH LABORATORY,[1] PEORIA, ILLINOIS]

Preparation and Reactions of Dialkoxytetrahydrofurans[2]

BY JØRGEN FAKSTORP,[3] DOLORES RALEIGH AND L. E. SCHNIEPP

The opening of the furan ring by means of hydrolytic agents has long attracted considerable interest. However, only in the case of methylfuran[4] and dimethylfuran[5] has hydrolytic cleavage led to results of any practical importance. The investigations of Meinel[6] and Clauson-Kaas and co-workers[7] resulting in methods for the preparation of stable dialkoxydihydrofurans which are cyclic acetals of unsaturated 1,4-dicarbonyl compounds and easily convertible into these, represent important advances in this field.

The procedures developed by these authors con-

---

[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

[2] Presented in part before the Division of Organic Chemistry at the 114th National Meeting of the American Chemical Society, Washington, D. C., August 30, 1948.

[3] American–Scandinavian Foundation Fellow 1947–1948.

[4] C. Harries, *Ber.*, **31**, 37 (1898).

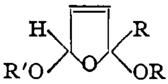
[5] F. Dietrich and C. Paal, *ibid.*, **20**, 1085 (1887).

[6] K. Meinel, *Ann.*, **510**, 129 (1934); **516**, 231 (1935).

[7] (a) N. Clauson-Kaas, *Kgl. Danske Videnskab. Selskab. Math.-Fys. Medd.*, **22**, [6] (1947), *C. A.*, **42**, 1930 (1948); (b) N. Clauson-Kaas and F. Limborg, *Acta Chem. Scand.*, **1**, 619 (1947); (c) N. Clauson-Kaas and J. Fakstorp, *ibid.*, **1**, 415 (1947); (d) N. Clauson-Kaas, F. Limborg and J. Fakstorp, *ibid.*, **2**, 109 (1948).

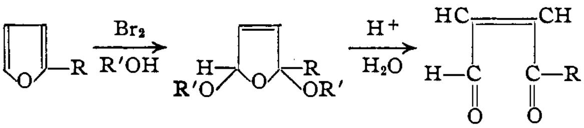
TABLE I

DIALKOXYDIHYDROFURANS



R	R′	Yield, %	B. p. °C.	Mm.	n_D^t	t	Empirical formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
H	C_2H_5	79.2	50–53	1	1.4310	25	$C_8H_{14}O_3$	Ref. 7a			
H	n-C_3H_7	42.4	84	3	1.4386	27	$C_{10}H_{18}O_3$	64.7	9.68	64.3	10.0
H	n-C_4H_9	64.6	102	2	1.4368	27	$C_{12}H_{22}O_3$	Ref. 7d			
CH_3	C_2H_5	65.7	88–92	3	1.4264	25	$C_9H_{16}O_3$	62.8	9.32	60.6	9.14
CH_2OH	C_2H_5	48.7	105	3	1.4519	26	$C_9H_{16}O_4$	57.5	8.52	57.7	8.55
$CH(OC_2H_5)_2$	C_2H_5	69.7	101	2	1.4343	27	$C_{13}H_{24}O_5$	60.0	9.24	59.9	9.18

sist in the reacting of a furan with bromine in an alcohol, preferably in the presence of a substance which will neutralize the hydrogen bromide formed in the reaction and at the same time exert a favorable salting-out effect (calcium carbonate, potassium acetate).

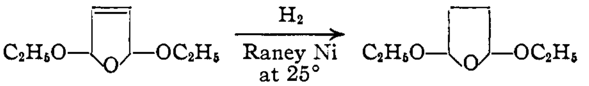


Since this method involves extraction with ether from a water solution (after salting out), it is inconvenient to handle large amounts and considerable skill is necessary to obtain good yields.

This paper describes a modification of the original procedure which will allow production on a larger scale and in improved yields. In this modified procedure the use of a neutralizing agent in the reaction mixture is eliminated and gaseous ammonia is used to neutralize the hydrohalide. Thus the formation of water or weak acids is avoided. After removal of the ammonium halide the solvent is removed and the residue distilled *in vacuo*. Chlorine has been used in lieu of bromine with good results. The procedure does not lend itself well to the alkoxylation of furfuryl alcohol since simultaneous reactions involving the side chain occur. In this case salting out, extracting with ether and drying gives a clean cut product (see Table I).[8]

The carbonyl compounds obtained by this procedure are unsaturated and are accordingly at a higher oxidation stage than those obtained by a hydrolytic cleavage of the furan ring. Hence, it was of interest to hydrogenate the dialkoxydihydrofurans to obtain well-defined, stable derivatives of the saturated 1,4-dicarbonyl compounds expected from direct hydrolysis of furan derivatives.

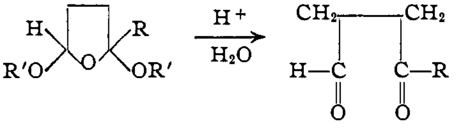
Earlier investigations[6] indicated that catalytic hydrogenation would result in products of hydrogenolysis rather than of hydrogenation. It was found, however, that Raney nickel was a suitable catalyst for hydrogenating the double bond in the 2,5-dialkoxydihydrofurans and that the hydrogenation should be carried out at room temperture.



I II

By using a Raney nickel catalyst at room temperature, diethoxydihydrofuran (I), dipropoxydihydrofuran, dibutoxydihydrofuran, diethoxydihydromethylfuran, diethoxydihydrofurfuryl alcohol and the ethylacetal of diethoxydihydrofurfural were hydrogenated to the corresponding tetrahydrofurans (Table II).

These hydrogenation products are colorless liquids which can be distilled *in vacuo* without decomposition. The lower members have pleasant flower-like odors. They are more stable to water and acids than the dialkoxydihydrofurans. However, they are hydrolyzed by boiling with aqueous solutions of mineral acids and the hydrolyzates react readily with carbonyl reagents to give good yields of derivatives of the corresponding 1,4-dicarbonyl compounds.



R = H (II)	R = H succinaldehyde
CH_3 (III)	CH_3 levulinaldehyde
CH_2OH (IV)	CH_2OH hydroxylevulinaldehyde
$CH(OC_2H_5)_2$ (V)	CHO α-ketoglutaraldehyde

The bis-phenylhydrazone, bis-semicarbazone and bis-oxime of succinaldehyde have been prepared from II and the physical constants are in agreement with those reported in the literature.

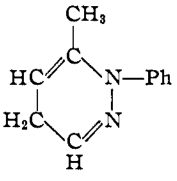
By heating II with dilute hydrochloric acid, neutralizing, salting out, and extracting with ether, followed by drying, evaporation of the ether, and distillation *in vacuo*, succinaldehyde was obtained in 30% yield.

The so-called "glassy" form of succinaldehyde, supposedly a polymer of low molecular weight, was encountered only after storing the sample for some time.

---

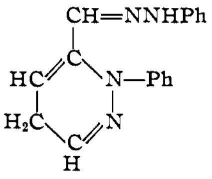
[8] After the conclusion of this work an abstract of a British patent (D. G. Jones, to Imperial Chemical Industries, British Patent 595,041, Nov. 25, 1947, *C. A.*, **42**, 2992 (1948)) dealing with the production of dialkoxydihydrofurans appeared. The procedure described therein is a modification of Meinel's procedure which has much in common with the one described above.

Isolation of the hydrolysis products of the substituted dialkoxytetrahydrofurans was not attempted. Diethoxytetrahydromethylfuran (III) was characterized by preparing the N-phenyldihydromethylpyridazine (VI) by its reaction with phenylhydrazine in the presence of mineral acid.



VI

Diethoxytetrahydrofurfuryl alcohol (IV) was characterized by the preparation of N-phenylformyl-dihydropyridazine phenylhydrazone (VII), formed under the same conditions as those just mentioned.

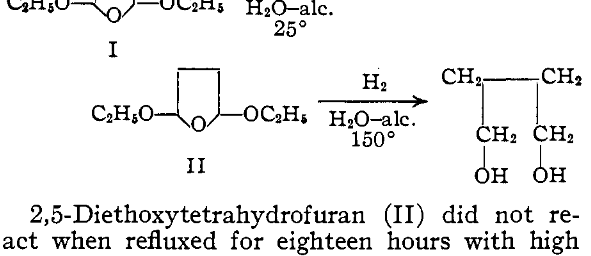


VII

The tris-semicarbazone of α-ketoglutaraldehyde obtained from the acetal of diethoxytetrahydrofurfural (V) was used as the characterizing derivative.

Since the 1,4-dicarbonyl compounds resulting from the hydrolysis of dialkoxytetrahydrofurans are difficult to obtain in a monomeric, water-free state, it was of interest to investigate the possibilities of using either the dialkoxytetrahydrofurans themselves, or the aqueous solutions of the 1,4-dicarbonyl compounds, as starting materials in various reactions.

Hence, diethoxydihydrofuran (II) was hydrogenated over Raney nickel in an alcohol–water or a dioxane–water mixture to give 1,4-butanediol in 50% yield. The reaction takes place in two distinct steps.



2,5-Diethoxytetrahydrofuran (II) did not react when refluxed for eighteen hours with high boiling primary and secondary amines, *e. g.*, decylamine or morpholine.

When II was heated in a water–alcohol mixture saturated with ammonia a small amount of pyrrole (5% of theoretical) was isolated; the major part of II was recovered unchanged. If the same reaction was carried out under reducing conditions (in the presence of Raney nickel and hydrogen) a mixture of pyrrole (approximately 10%)and pyrrolidine (approximately 7%) together with unreacted II was obtained. A still higher but not satisfactory yield of pyrrole and pyrrolidine was obtained when the ammonolysis was carried out with prehydrolyzed II or, in other words, with a solution of succinaldehyde.

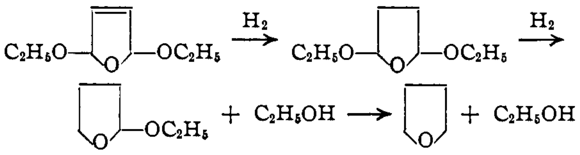
Attempts to prepare 1,4-diaminobutane by carrying out the ammonolysis in the presence of ammonium chloride[9] were unsuccessful.

The dialkoxytetrahydrofurans heated with resorcinol in the presence of a catalytic amount of acid in an alcohol–water mixture formed clear, almost colorless, tough resins.

In the search for a suitable hydrogenation catalyst, several were found to give mixtures of hydrogenation and hydrogenolysis products.

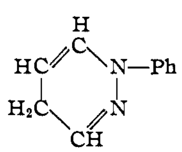
The amounts of 2,5-diethoxytetrahydrofuran (II) and of lower and higher boiling fractions obtained by hydrogenation of 2,5-diethoxy-2,5-dihydrofuran (I) over various catalysts are shown in Table III.

Hydrogenation over Raney nickel at 150°, in the absence of solvent, resulted in the formation of ethanol, tetrahydrofuran and 2-ethoxytetrahydrofuran along with the expected 2,5-diethoxytetrahydrofuran (II). Isolation of these products suggests that the hydrogenolysis proceeds according to the scheme



Hydrogenation over copper chromite catalyst at 200° gave, in addition to II, a small amount of a low-boiling material whose properties indicated that it might be 2,5-dihydrofuran. The greater portion of the product in this case was resinous material.

The high-boiling products obtained in considerable amounts from the hydrogenation of I over platinum and palladium catalysts were obviously mixtures and all attempts at separation and characterization were unsuccessful. Acid hydrolysis followed by treatment with phenylhydrazine gave a small yield of N-phenyldihydropyridazine (VIII)[10] showing the presence of II in the mixture.



VIII

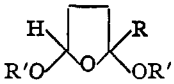
---

[9] E. R. Alexander and A. L. Misegades, THIS JOURNAL, **70**, 1315 (1948).

[10] C. Ciamician and C. U. Zanetti, *Ber.*, **23**, 1784 (1890).

TABLE II

DIALKOXYTETRAHYDROFURANS



R	R′	B. p. °C.	Mm.	$n^{25}D$	d^{25}_4	M_D Calcd.	M_D Obs.	Empirical formula
H	C_2H_5	30–31	1	1.4164	0.9598	41.97	41.87	$C_8H_{16}O_3$
H	n-C_3H_7	47–48	1	1.4227	.9268	51.11	51.62	$C_{10}H_{20}O_3$
H	n-C_4H_9	107–110	6	1.4281	.9251	60.35	60.14	$C_{12}H_{24}O_3$
CH_3	C_2H_5	44–47	1	1.4273	.9398	46.49	46.84	$C_9H_{18}O_3$
CH_2OH	C_2H_5	85–86	1	1.4401	1.0537	48.01	47.53	$C_9H_{18}O_4$
$CH(OC_2H_5)_2$	C_2H_5	93–95	1	1.4238	0.9766	68.25	68.42	$C_{13}H_{26}O_5$

Experimental

Alkoxylation of Furans

(A) **Furan.**—Thirty-six ml. (0.5 mole) of freshly distilled furan, 100 ml. of absolute ether and 150 ml. of ethanol dried over magnesium were placed in a 1-liter, three-necked flask equipped with stirrer, thermometer, soda lime tube and dropping funnel and cooled to −35°.

Bromine, 28 ml. (0.5 mole), dissolved in 350 ml. of cold alcohol (−40°) was added with stirring at such a rate that the temperature did not exceed −25°. After addition was complete, stirring was continued for twenty minutes. Ammonia was bubbled through the reaction mixture until the reaction on test paper was only slightly acid. Stirring was continued at −5° until complete disappearance of color. Enough ammonia to make the reaction mixture slightly alkaline was added.

Removal of ammonium bromide by filtration, and of solvents by distillation at reduced pressure, left a residue which upon distillation *in vacuo* yielded the diethoxydihydrofuran. An additional 10% of material could be obtained by distilling the removed solvents through a packed column and distilling the residue *in vacuo* as above (Table I). Dipropoxy- and dibutoxydihydrofurans were prepared in the same manner by using n-propanol and n-butanol instead of ethanol.

(B) **Substituted Furans.**—Methylfuran and furfuryl alcohol were treated with bromine and ethanol at −50°. Ammonia was added immediately after the bromine addition was complete. Diethoxydihydromethylfuran was isolated in the usual manner. Diethoxydihydrofurfuryl alcohol was isolated as follows: The contents of the reaction flask after stirring for one hour at −5° were poured into a 3-liter separatory funnel containing 500 ml. of a saturated sodium chloride solution, 175 g. of cracked ice and 800 ml. of distilled ether. After separation, the water layer was extracted once more with 200 ml. of ether. The combined extracts were dried with three portions of anhydrous potassium carbonate of 100 g. each. After removal of solvents the remainder was distilled *in vacuo*.

Furfural was treated with bromine in ethanol at −5° and the reaction mixture worked up in accordance with the procedure described under (A). Distillation gave two main fractions, one boiling at 62–64° (3 mm.) (18.7%) which was the diethylacetal of furfural, and a higher boiling one which was the diethoxy adduct (Table I).

(C) **Alkoxylation with Chlorine.**—The furan was dissolved in 100 ml. of ether and 200 ml. of ethanol. Chlorine, 35.46 g. (0.5 mole) was added from a small chlorine tank mounted on a balance. The reaction temperature was −20°. The reaction mixture was worked as described under (A).

Hydrogenation of Dialkoxydihydrofurans

Apparatus.—The low-pressure hydrogenations were carried out in a hydrogenation apparatus of the shaking-bottle type. For the high-pressure work an apparatus of the rocking-bomb type with a total volume of 310 ml. was used.

Catalysts.—(a) Raney nickel was prepared in the usual manner from 125 g. of alloy at 50° and washed 18 times by decantation with 1-liter portions of water. Most of the water was removed by centrifuging and washing with alcohol in which the catalyst was ultimately stored.

(b) Copper chromite was prepared by the procedure of Adkins.[11]

(c) Palladium (5% on barium sulfate) was prepared as follows: Freshly precipitated barium sulfate was dispersed in hot water in which palladous chloride dihydrate had been dissolved by means of dilute hydrochloric acid. The palladium oxide was precipitated by 10% sodium hydroxide. After filtration the precipitate was washed chloride-free, dried and reduced immediately before use.

(d) The platinum oxide catalyst was a purchased material and used as such or reduced immediately before use.

General Procedure.—Hydrogenations were carried out on 0.1- or 0.2-mole samples of the dialkoxydihydrofurans with or without solvent. Solvents were alcohol, dried over magnesium, or dioxane, dried over potassium hydroxide and silica gel. In the cases where solvents were used the hydrogenation mixture was made up to a total volume of 150 ml. After hydrogenation the reaction mixtures were shaken with a small amount of a drying agent to eliminate any possibility of hydrolysis during the further treatment. Diethoxydihydrofuran (I), dipropoxy- and dibutoxydihydrofurans were hydrogenated at low pressure, the substituted dialkoxydihydrofurans at high pressure and room temperature.

Hydrogenolysis of diethoxydihydrofuran over platinum and palladium catalysts was carried out at an initial pressure of about 50 p. s. i. and at room temperature, over Raney nickel and copper chromite at an initial pressure of about 2000 p. s. i. and at temperatures between 100° and 200°.

Diethoxytetrahydrofuran (II).—Diethoxydihydrofuran (I) 79 g. (0.5 mole), was hydrogenated over 3 ml. of Raney nickel. The hydrogen uptake was complete in forty minutes. After removal of the catalyst by filtration, II was distilled *in vacuo*. The weight of product was 68 g., 85% of the theoretical.

Succinaldehyde.—A mixture of diethoxytetrahydrofuran (II) 16 g. (0.1 mole) and 80 ml. of 0.6 N hydrochloric acid was heated until complete solution occurred. Sodium bicarbonate was then added in very slight excess. The succinaldehyde was salted out by excess calcium chloride and extracted with 150 ml. of ether. The ether layer was dried with two portions of 25 g. each of magnesium sulfate. The ether was removed by distillation through a helices-packed column and the residue distilled *in vacuo*. The main fraction boiled at 54–58° (14 mm.) and two redistillations gave 2.7 g. of the aldehyde, b. p. 62° (14 mm.) (30% yield).

Anal.[12] Calcd. for $C_4H_6O_2$: C, 55.7; H, 6.95. Found: C, 56.3; H, 6.92.

This product gave the "pyrrole test" with ammonia, a bis-oxime melting at 169° and a bis-phenylhydrazone melting at 117°.

---

[11] H. Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wis., 1937.

[12] All analyses were microdeterminations by C. H. Van Etten and Mary B. Wiele of this Laboratory. All melting points were determined on a Kofler hot stage and the temperatures at which the crystals began to disintegrate are reported.

TABLE II (*Continued*)

Analyses, %				Derivatives[a]							
Calcd.		Found		M. p.,	Yield,	Analyses, %					
						Calcd.			Found		
C	H	C	H	°C.	%	C	H	N	C	H	N
59.9	10.00	59.9	9.96	122[b]	62[h]	72.2	6.76	21.1	71.9	6.63	21.1
63.8	10.63	60.9	9.18	169[c]	72[h]	..	..	24.6	..	..	24.6
66.7	11.11	67.5	11.30	192[d]	61[h]	..	..	41.8	..	..	41.8
62.1	10.34	62.1	9.72	193[e]	82	..	..	16.3	..	..	16.3
56.9	9.47	57.6	9.44	237[f]	92	73.9	5.80	20.28	73.2	5.78	..
59.5	9.92	59.0	9.66	225[g]	58	33.6	5.26	44.2	33.4	5.57	43.7

[a] Of dicarbonyl compounds produced on hydrolysis. [b] Bis-phenylhydrazone of succinaldehyde, recrystallized from alcohol. C. Harries, *Ber.*, **34**, 1497 (1904), reports m. p. 124°. [c] Bis-oxime of succinaldehyde, recrystallized from water. R. Willstätter and W. Heubner, *Ber.*, **40**, 3871 (1907), report m. p. 171°. [d] Bis-semicarbazone of succinaldehyde. C. Harries and H. Krützfeld, *Ber.*, **39**, 3671 (1906), report m. p. 188°. [e] Phenyldihydromethylpyridazine (VI), recrystallized from alcohol. C. Harries, *Ber.*, **31**, 45 (1898); **42**, 442 (1909), reports m. p. 197°. [f] Phenylformyldihydropyridazine phenylhydrazone (VII), recrystallized from pyridine. [g] Tris-semicarbazone of α-keto-glutaraldehyde recrystallized from water–alcohol mixture. [h] From diethoxytetrahydrofuran.

TABLE III

HYDROGENATION AND HYDROGENOLYSIS PRODUCTS FROM 2,5-DIETHOXYDIHYDROFURAN (I)

Catalyst	Temp., °C.	H_2 absorbed, moles/mole	Solvent	Fractions on distillation (wt. %) <100°	100–120°	30–35° (1 mm.)[a]	>35° (1 mm.)	Residue
PtO_2	25	1.0	Ethanol	...	...	56	35	9
PtO_2	25	1.54	None	5	5	38	40	12
Pd (5% on $BaSO_4$)	25	1.0	Dioxane	5	...	55	40	..
CuCrO	200	2.8	Dioxane	10[b]	8	35	..	47
Raney Ni	150	2.5	None	20[c]	10[d]	50	20	..
Raney Ni	25	1.0	None	5	...	85	5	5

[a] 2,5-Diethoxytetrahydrofuran (II). [b] Mixture of ethanol and a material of b. p. 69–70°, $n^{25}D$ 1.4268. [c] Mixture of ethanol and tetrahydrofuran. [d] Refractionated to yield 2-ethoxytetrahydrofuran, b. p. 113–116°.

Derivatives of 1,4-Dicarbonyl Compounds from the Dialkoxytetrahydrofurans in Table II.—Except for the bis-phenylhydrazone of succinaldehyde, which was prepared by hydrolyzing II with glacial acetic acid, and the bis-oxime of the same aldehyde obtained by hydrolyzing II with hydroxylamine hydrochloride, the derivatives used for characterization of the dialkoxytetrahydrofurans were prepared from 0.01 mole hydrolyzed with 5 ml. of 0.1 *N* hydrochloric acid by boiling for two minutes followed by addition of the particular reagent made up in the usual manner.

1,4-Butanediol.—The hydrogenation was carried out on 0.2 mole of (I) or (II) dissolved in 115 ml. of a mixture of 80% dioxane and 20% water. In the case of (I), 0.2 mole of hydrogen was absorbed at room temperature. Heating to 150° in the rocking-bomb hydrogenation apparatus resulted in the absorption of another 0.4 mole in both cases. The absorption was complete in five hours. The catalyst was removed and the mixture distilled through a Widmer column to remove the dioxane–water azeotrope which distilled at 87.5°. The residue was dried with potassium carbonate, filtered and distilled *in vacuo*. Ten grams (56%) of 1,4-butanediol, b. p. 82–84° (2 mm.), $n^{25}D$ 1.4466 was obtained.

Anal. Calcd. for $C_4H_{10}O_2$: C, 53.3; H, 11.11. Found: C, 53.3; H, 11.11.

Bis-carbanilate, m. p. 178° (from xylene), reported m. p. is 183°,[13] bis-N-(α-naphthyl)-carbamate, m. p. 197° (from xylene), reported m. p. is 198°.[14]

Pyrrole and Pyrrolidine.—Sixteen grams of II (0.1 mole), 60 ml. of concentrated ammonium hydroxide, 10 ml. of water and 30 ml. of ethanol saturated with ammonia was charged into a hydrogenation bomb and hydrogenated over Raney nickel at 90° at an initial pressure of 1600 p. s. i. for four hours. Only a slight pressure drop was observed. The contents of the bomb were filtered and refluxed for two hours to remove excess ammonia and was then extracted with three 150-ml. portions of ether after addition of 200 ml. of water. The ether extracts were combined and dried. Distillation through a packed column gave 18 ml. of a mixture of ethanol, water and pyrrolidine.

The residue was distilled at reduced pressure and 2.4 g. (35%) of pyrrole boiling at 34° at 10 mm. was collected; $n^{25}D$ 1.5068.

Anal. Calcd. for C_4H_5N: C, 71.7; H, 7.46; N, 20.9. Found: C, 71.7; H, 7.33; N, 21.1.

Near the end of the distillation the temperature rose to 55° and about 4 g. of II was recovered. The pyrrolidine-containing fraction was treated with excess hydrochloric acid and evaporated. To the residue was added 10% sodium hydroxide solution and 100 ml. of ether. After drying, the ether was evaporated and the pyrrolidine distilled at normal pressure; yield 2 g., 28%, b. p. 85–88°; picrate, m. p. 108°, reported 112°.[15]

Anal. Calcd. $C_4H_9N{\cdot}C_6H_3N_3O_7$: N, 18.7. Found: N, 18.6.

Products of Hydrogenolysis.—When 2,5-diethoxydihydrofuran (I) was hydrogenated over Raney nickel at 150°, 2.5 moles of hydrogen per mole were absorbed. The low-boiling portion of the reaction mixture (Table III) was refractionated twice and a fraction boiling at 69–76° obtained. This material was treated with sodium, the volatile matter distilled, and the treatment repeated until no further reaction with sodium occurred. The distillate was probably tetrahydrofuran (b. p. 68°, $n^{25}D$ 1.4074). The other constituent of the fraction was shown to be ethanol by the preparation of its N-(α-naphthyl)-carbamate, m. p. 96°.

Fractional distillation of that portion of the reaction

---

(13) A. Müller, *Monatsh.*, **49**, 29 (1928).

(14) W. R. Kirner and G. H. Richter, THIS JOURNAL, **51**, 2505 (1928).

(15) S. Gabriel, *Ber.*, **24**, 3234 (1891).

mixture having a boiling range of 100–120° gave a main fraction which distilled at 113–116°; $n^{25}D$ 1.4055, d^{25}_4 0.9225. This material had a menthol-like odor and reacted with 2,4-dinitrophenylhydrazine reagent to give a derivative of m. p. 116° which analyzed correctly for the dinitrophenylhydrazone of γ-hydroxybutyraldehyde. Wilson[16] reported this compound as melting at 116–117°.

Anal. Calcd. for $C_{10}H_{12}O_5N_4$: N, 20.9. Found: N, 21.1.

On the basis of this evidence and the close agreement of the calculated and found molecular refractivities (calcd. 30.99; found, 30.86), this product is believed to be 2-ethoxytetrahydrofuran.

The low-boiling (69–70°) fraction from the hydrogenation of I over copper chromite at 200° contained very little ethanol and had a higher refractive index ($n^{25}D$ 1.4268) than tetrahydrofuran. Treatment with bromine in chloroform indicated the presence of unsaturated material. Attempted hydrolysis with acid followed by treatment with carbonyl reagents gave no derivatives. No definite products were isolated.

Hydrogenation of (I) over palladium on barium sulfate gave appreciable amounts of materials boiling higher than the normal hydrogenation product II. Hydrolysis of 1 ml. of this material with 0.6 *N* hydrochloric acid followed by treatment with 1 ml. of phenylhydrazine in 7 ml. of 15% acetic acid gave a small amount N-phenyldihydropyridazine (IX), m. p. 183–184°.[10]

Anal. Calcd. for $C_{10}H_{10}N_2$: C, 75.9; H, 6.33; N, 17.7. Found: C, 75.8; H, 6.28; N, 17.7.

Summary

1. The preparation of 2,5-dialkoxytetrahydrofurans by catalytic hydrogenation of the corresponding dihydrofurans is described.

2. 2,5-Diethoxytetrahydrofuran is shown to be convertible to succinaldehyde, 1,4-butanediol, and, in low yield, to pyrrole and pyrrolidine.

3. Several 2-substituted-2,5-diethoxytetrahydrofurans were also prepared and characterized by conversion to derivatives of the corresponding 1,4-dicarbonyl compounds.

4. Some evidence is given to show that ethanol, tetrahydrofuran and 2-ethoxytetrahydrofuran are formed on hydrogenolysis of 2,5-diethoxy-2,5-dihydrofuran.

PEORIA, ILL. RECEIVED MAY 19, 1949

---

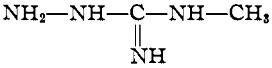
[16] C. L. Wilson, *J. Chem. Soc.*, 56 (1945).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

1-Methyl-1-aminoguanidine[1]

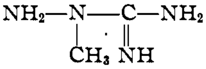
BY ALBERT H. GREER[2] AND G. B. L. SMITH[3]

In the course of the investigation of the preparation of the isomers of sulfanilylmethylaminoguanidine it was found necessary to prepare the three possible structural isomers of methylaminoguanidine. These isomers can be assigned the structures

(I) 

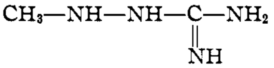
$NH_2—NH—C(=NH)—NH—CH_3$

3-Methyl-1-aminoguanidine

(II) 

$NH_2—N(CH_3)—C(=NH)—NH_2$

1-Methyl-1-aminoguanidine

(III) 

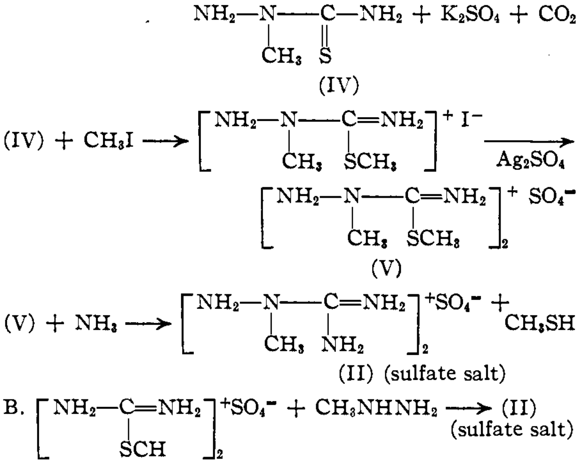
$CH_3—NH—NH—C(=NH)—NH_2$

1-Methylamidoguanidine

Isomer (I) has been reported in the literature.[4] The present paper describes the preparation and character of Isomer (II) in the form of its sulfate salt. Isomer (III) is now under investigation.

Isomer (II) as its sulfate salt has been prepared according to two procedures

A. $CH_3NHNH_2{\cdot}H_2SO_4 + KSCN + K_2CO_3 \xrightarrow[165°]{\Delta}$



$$NH_2—N(CH_3)—C(=S)—NH_2 + K_2SO_4 + CO_2 \quad \text{(IV)}$$

$$\text{(IV)} + CH_3I \longrightarrow \left[NH_2—N(CH_3)—C(SCH_3)=NH_2\right]^+ I^- \xrightarrow[Ag_2SO_4]{} \left[NH_2—N(CH_3)—C(SCH_3)=NH_2\right]^+_2 SO_4^= \quad \text{(V)}$$

$$\text{(V)} + NH_3 \longrightarrow \left[NH_2—N(CH_3)—C(NH_2)=NH_2\right]^+_2 SO_4^= + CH_3SH \quad \text{(II) (sulfate salt)}$$

$$\text{B.}\ \left[NH_2—C(SCH)=NH_2\right]^+_2 SO_4^= + CH_3NHNH_2 \longrightarrow \text{(II) (sulfate salt)}$$

Evidence for the configuration of (IV) is given by the formation of a benzylidene derivative. According to the nature of the reaction[5] this indicates that (IV) contains a primary hydrazine amino group. The reaction does not take place with the —NH_2 of the amide group. It is reasonable to assume that in the formation of (IV), the nitrogen atom adjacent to the methyl group of methylhydrazine is the more basic and it would appear that this reaction consists of a nucleophilic attack by methylhydrazine on the carbon atom of thiocyanic acid or thiocyanate anion

---

[1] Abstracted from part of the thesis submitted by Albert H. Greer to the Graduate Faculty in partial fulfillment of the Ph.D. degree in Chemistry, 1949.

[2] Present address: The Permutit Co., Birmingham, New Jersey.

[3] Present address: Chemistry Division, Research Dept., U. S. Naval Ordnance Test Station (Inyokern), China Lake, Calif.

[4] Kirsten and Smith, THIS JOURNAL, **58**, 800 (1936).

[5] Thiele and Bilian, *Ann.*, **302**, 299 (1898).