

## The Acyloxylation of Furan with Lead Tetraacyloxylates; *Cis-Trans* Isomerism of 2,5-Diacyloxy-2,5-dihydrofurans and 2,5-Diacyloxytetrahydrofurans

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The formation of 2,5-diacetoxy-2,5-dihydrofuran from furan and lead tetraacetate has been previously reported (yield 45 per cent)<sup>1</sup>. We have now worked out new directions for this synthesis, in order that larger amounts of diacetoxydihydrofuran can be more easily prepared (yield 70 per cent).\*

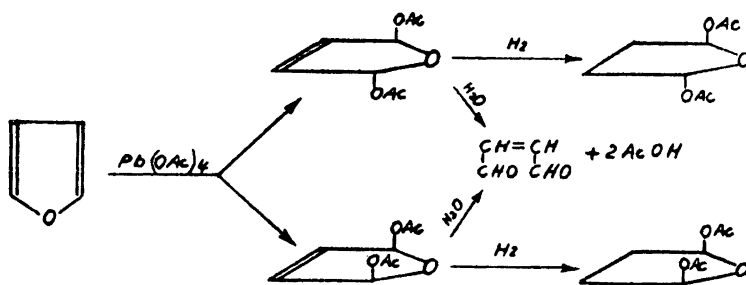
Diacetoxydihydrofuran, prepared by the lead salt method, is usually obtained as a liquid, but we have found that it consists 1/3 of a crystalline isomer and 2/3 of another isomer, which it was not possible to bring to crystallization. The two isomers can be easily separated by crystallization from methanol. It was shown by hydrolysis and identification of malealdehyde, that both compounds actually are 2,5-diacetoxy-2,5-dihydrofurans. They must therefore be *cis-trans* isomers. We do not yet know, which of the compounds is the *cis*, and which the *trans* isomer.

Diacetoxydihydrofuran, prepared by the bromine method<sup>2</sup>, also crystallizes readily from methanol, and was found to consist about half of the crystalline isomer. No analytically pure liquid isomer could be isolated. It is quite reasonable that the two *cis-trans* isomers are formed in different proportions by the two different methods of preparation.

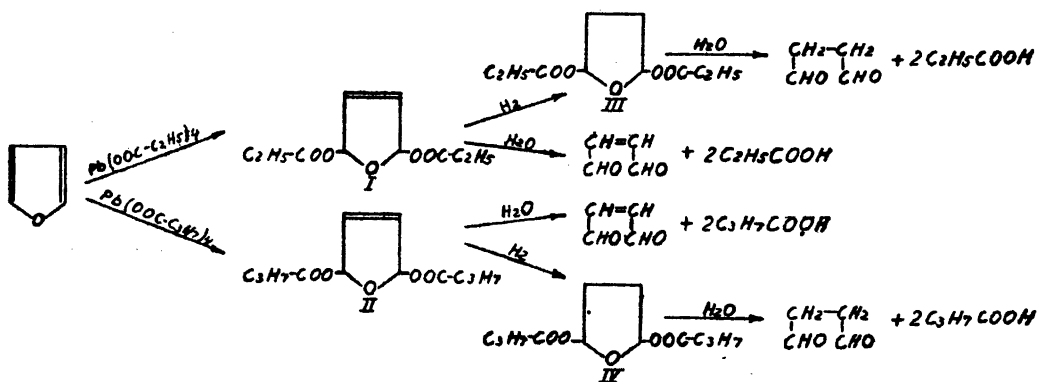
The diacetoxydihydrofurans were hydrogenated catalytically to the corresponding 2,5-diacetoxytetrahydrofurans (*cf.* <sup>2</sup>). Crystalline diacetoxydihydrofuran gave a crystalline tetrahydrofuran, and liquid diacetoxydihydrofuran gave a liquid tetrahydrofuran. Naturally the two diacetoxytetrahydrofurans must also be *cis-trans* isomers,

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\* Patent pending.



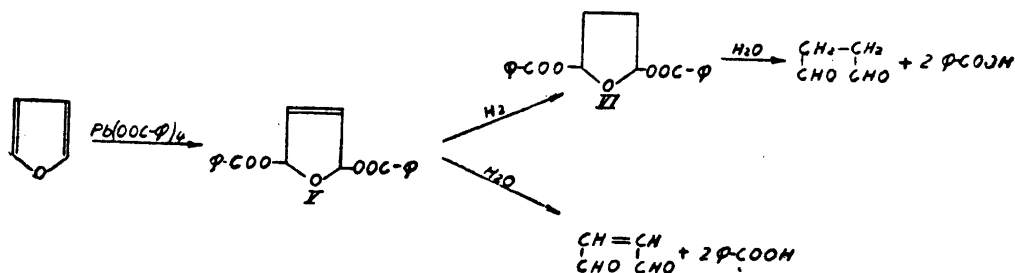
We have also synthesized the homologous 2,5-dipropionyxy- and 2,5-dibutyroxy-2,5-dihydrofurans (I and II) from furan and the corresponding lead tetraacyloxyates. These are all new compounds. Their structure was proved by hydrolysis and identification of malealdehyde and propionic, respectively butyric acid. Catalytic hydrogenation of I and II gave 2,5-dipropionyxy- and 2,5-dibutyroxytetrahydrofuran (III and IV), which are also new compounds. Hydrolysis of III and IV gave succinaldehyde.



Dipropionyxydihydrofuran was, like diacetoxydihydrofuran, found to consist of a liquid and a crystalline isomer (in proportion ca. 1 : 3), which were shown to be *cis-trans* isomers by hydrolysis to malealdehyde. Hydrogenation of the two isomers gave the two corresponding *cis-trans* isomeric dipropionyxytetrahydrofurans. The dipropionyxytetrahydrofuran obtained from crystalline dipropionyxydihydrofuran was also crystalline.

Dibutyroxydihydrofuran was obtained as a liquid. It crystallized after standing with a little ether at  $-20^\circ$  for several months (melting point  $-3$  to  $1^\circ$ ) and appears to consist almost entirely of either the *cis* or the *trans* isomer.

Finally 2,5-dibenzoxy-2,5-dihydrofuran (V) was prepared from furan and lead tetrabenzoate. Hydrolysis gave benzoic acid, but no malealdehyde could be isolated, probably because the sensitive aldehyde was destroyed during the prolonged boiling, which was necessary to hydrolyze this dihydrofuran. Hydrogenation gave 2,5-dibenzoxytetrahydrofuran VI, which was hydrolyzed to succinaldehyde.



V and VI are both new compounds. Their structure is proved by the above reactions.

2,5-Dibenzoxy-2,5-dihydrofuran was obtained as a crystalline solid, which melted at  $179-182^\circ$  after one crystallization from dioxane. After two more crystallizations the melting point of the product remained constant ( $185-190^\circ$ ). The crude, as well as the pure product and the intermediate fractions were, however, analytically pure. Therefore dibenzoxydihydrofuran may also be a mixture of the *cis* and the *trans* isomer.

## EXPERIMENTAL

Microanalyses by Franz Limborg

### 2,5-Diacetoxy-2,5-dihydrofuran

**Preparation.** 580 ml of glacial acetic acid and 230 ml of acetic anhydride are placed in a 1-liter 3-necked flask provided with a stirrer, a thermometer and a reflux condenser with a calcium chloride tube. 300 g of red lead oxide (0.44 mole) is added to the stirred solution in portions of  $15-20 \text{ g}^3$ . The temperature is kept at  $50^\circ$  by external heating. The addition takes about  $3 \frac{1}{2}$  hours and part of the lead tetraacetate formed, precipitates as white crystals. 29.8 g of furan (0.44 mole) (note 1) is added, the temperature raised to  $60^\circ$  and heating discontinued. In the course of the following 10 minutes the temperature rises to  $65^\circ$ . The reaction mixture is then kept at  $60-65^\circ$  for 75 minutes, first by occasional cooling, later by external heating. The mixture is now a clear, pale-yellow solution (note 2). The major part of the solvent is distilled under 10 mm from a water-bath of  $60-65^\circ$  and 400 ml of anhydrous ether is added to the pasty residue. The mixture is shaken for some minutes and then stirred vigorously whereby the precipitate becomes

readily filterable. The lead acetate is filtered off on a sintered glass-disk and washed with 100 ml of anhydrous ether. Yield 415 g of lead acetate = 97 %.

The yellowish-brown filtrate is distilled from a water-bath of 70°, finally in vacuum, and the residue distilled further in vacuum. After 15–20 g of a pale-yellow fore-run (b.p.<sub>10</sub> < 127°), the main fraction is collected. Yield 56.0 g of diacetoxydihydrofuran = 69 %; pale-yellow liquid (note 3), b.p.<sub>0.5</sub> = 89–93°;  $n_D^{25} = 1.4536$  (all refractive indices reported in this communication are only accurate within  $\pm 0.0008$ ).

*Separation into two isomers.* Diacetoxydihydrofuran may be crystallized from various solvents. Crystals are formed rapidly from solutions in methanol, ethanol, ether and petroleum ether, and slowly from ethyl acetate and carbon tetrachloride. Methanol was found to be the best solvent for the separation of the liquid and the crystalline diacetoxydihydrofuran.

(1). 20.0 g of the above sample of diacetoxydihydrofuran was crystallized from 20 ml of anhydrous methanol at  $-20^\circ$  under anhydrous conditions; yield 7.0 g of crystals. Recrystallization from 7 ml of methanol gave 6.3 g of crystalline diacetoxydihydrofuran; m.p. 51–52° (Hershberg apparatus, corr.);  $n_D^{25} = 1.4541$  (after melting).

$C_8H_{10}O_5$ (186.2)	Calc.	C 51.6	H 5.4
	Found	» 51.4	» 5.5

A sample of crystalline diacetoxydihydrofuran was stored in a sealed glass tube at room temperature. The crystals became slightly sticky after 3–4 months.

The methanol was distilled from the mother liquor from the first crystallization and the residue distilled in vacuum. Yield 12.0 g; b.p.<sub>0.2</sub> = 84–87°;  $n_D^{25} = 1.4542$ . The product was dissolved in 12 ml of methanol and kept for 3 hours at  $-20^\circ$ . No crystals were formed. Cooling for 2 hours at  $-80^\circ$  gave 0.4 g of crystals, which were filtered off. The methanol was distilled from the mother liquor and the residue distilled in vacuum. Yield 11.0 g of liquid diacetoxydihydrofuran; b.p.<sub>0.2</sub> = 84–87°;  $n_D^{25} = 1.4545$ .

	Found	C 51.7	H 5.4
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A sample of liquid diacetoxydihydrofuran was kept for 4 months with occasional scratching. No crystals were formed.

(2). 20.0 g of diacetoxydihydrofuran, prepared by the bromine method<sup>2</sup> (positive Beilstein test for halogen) was crystallized from 20 ml of methanol as above. Yield after 3 hours 6.5 g of crystals; m.p. 49–51°. After 24 hours another 7 g of a partially crystalline product had separated; m.p. < 20°. Both fractions as well as their mother liquors gave a positive Beilstein test. The first crop of crystals (6.5 g) was recrystallized from 7 ml of methanol. Yield 5.9 g of crystalline diacetoxydihydrofuran, m.p. 50.5–52.0°. The product gave a negative Beilstein test. Repeated crystallization did not give a higher melting product.

	Found	C 51.7	H 5.4
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*Crystalline isomer; hydrolysis and identification of malealdehyde.* 46.2 mg of crystalline diacetoxydihydrofuran was shaken for 30 minutes with 1 ml of N/10 sulfuric acid. A solution of 0.20 ml of phenylhydrazine and 0.50 ml of acetic acid in 10 ml of water was added and the mixture shaken vigorously. After 15 minutes the precipitate was filtered off, washed thoroughly with water and dried. The product was crystallized from acetone-benzene and dried (sulfuric acid, 0.05 mm, 20°, 0.5 hours). Yield 38.7 mg of malealdehyde bis-phenylhydrazone = 59 %; m.p. 168–170° (Kofler stage, corr.); previously found<sup>4</sup> 171°.

$C_{16}H_{16}N_4$ (264.3)	Calc.	N 21.2
	Found	» 20.9

*Crystalline isomer; hydrogenation.* 1.60 g of crystalline diacetoxydihydrofuran and 8 ml of anhydrous ethanol were shaken with 0.2 g of Raney nickel under 100 atmospheres of hydrogen for 2 hours at room temperature. After filtration the ethanol was distilled in vacuum from a water-bath and the residue distilled further in vacuum. After 0.29 g of fore-run (b.p.<sub>0.3</sub> = 84°) the main fraction is collected. Yield 1.14 g of diacetoxytetrahydrofuran = 71 %; b.p.<sub>0.3</sub> = 84–86°; m.p. 18–21°;  $n_D^{25} = 1.4371$ .

$C_8H_{12}O_5$ (188.2)	Calc.	C	51.1	H	6.4
	Found	»	51.3	»	6.6

*Liquid isomer; hydrolysis and identification of malealdehyde.* 61.8 mg of liquid diacetoxydihydrofuran was hydrolyzed as described above. Yield 53.5 mg of malealdehyde bisphenylhydrazone = 61 %; m.p. 171–172°.

$C_{16}H_{16}N_4$ (264.3)	Calc.	N	21.2
	Found	»	21.2

*Liquid isomer; hydrogenation.* 2.00 g of liquid diacetoxydihydrofuran was hydrogenated as above. Fore-run 0.17 g; b.p.<sub>0.3</sub> = 84°. Yield 1.54 g of diacetoxytetrahydrofuran = 76 %; b.p.<sub>0.3</sub> = 84–87°;  $n_D^{25} = 1.4386$ . The product did not crystallize on standing at –20° for several weeks.

$C_8H_{12}O_5$ (188.2)	Calc.	C	51.1	H	6.4
	Found	»	51.2	»	6.5

### 2,5-Dipropionyloxy-2,5-dihydrofuran

*Preparation; method 1.* 58 g of lead tetrapropionate (0.115 mole) (note 4), 150 ml of propionic acid and 7.9 g of furan (0.115 mole) (note 5) are placed in a 3-necked round-bottomed flask provided with a stirrer, a thermometer and a reflux condenser with a calcium chloride tube. The temperature is raised to 55° and heating is discontinued. In the course of the following 10 minutes the temperature remains at 55°, and the reaction mixture is then kept at 55–60° for 35 minutes and at 60–65° for 45 minutes by external heating. The mixture is now a clear pale-yellow solution. The major part of the solvent is distilled under 10 mm from a water-bath of 60–70° and 250 ml of anhydrous ether is added to the residue. The mixture is shaken for some minutes and then stirred vigorously whereby the precipitate becomes readily filterable. The lead propionate is filtered off on a sintered glass-disk and washed with 100 ml of anhydrous ether.

The yellow filtrate is distilled in vacuum from a water-bath of 70° and the residue distilled further in vacuum. After 17.5 g of a pale-yellow fore-run (b.p.<sub>0.4</sub> < 97°), the main fraction is collected. Yield 19.0 g of dipropionyloxydihydrofuran = 76 %; pale-yellow liquid, b.p.<sub>0.4</sub> = 97–103°;  $n_D^{25} = 1.4510$ .

18.5 g of the product was redistilled. After 1.0 g of fore-run (b.p.<sub>0.3</sub> = 94°) the main fraction was collected. Yield 17.0 g; pale-yellow liquid, b.p.<sub>0.3</sub> = 94–98°;  $n_D^{25} = 1.4517$ . The product crystallized almost completely after inoculation.

$C_{10}H_{14}O_5$ (214.2)	Calc.	C	56.1	H	6.6
	Found	»	56.3	»	6.8

*Preparation; method 2.* 150 ml of propionic acid and 54 ml of propionic anhydride (technical product) are placed in a 3-necked flask provided with a stirrer, a thermometer and a reflux-condenser with a calcium chloride tube. 68.6 g of red lead oxide (0.100 mole) is added in the following manner. 10 g is added at 50° and the mixture is stirred for 4 hours at 50°. Then another 10 g is added at room temperature, and stirring is continued for 4 hours at room temperature. Finally the rest of the red lead oxide is added and

stirring is continued overnight. The next day a white precipitate of lead tetrapropionate has formed. The supernatant liquid has a faintly pink colour. The temperature is raised to 55° and 6.8 g of furan (0.100 mole) is added. Heating is discontinued. In the course of the following 10 minutes the temperature remains at 55°. The reaction mixture is then kept at 55–60° for 35 minutes and at 60–65° for 45 minutes by external heating. The major part of the solvent is distilled under 10 mm from a water-bath of 60–70° and 300 ml of anhydrous ether is added to the residue. The mixture is shaken for some minutes and then stirred vigorously whereby the precipitate becomes readily filterable. The lead propionate is filtered off on a sintered glass-disk and washed with anhydrous ether. Yield 104 g of lead propionate = 98 %.

The yellow filtrate is distilled from a water-bath, finally in vacuum, and the residue distilled further in vacuum. After 27 g of fore-run (b.p.<sub>0.1</sub> < 88°), the main fraction is collected. Yield 11.5 g of dipropionoxydihydrofuran = 54 %; pale-yellow liquid, b.p.<sub>0.1</sub> = 88–92°;  $n_D^{25} = 1.4520$ . The product crystallizes almost completely after inoculation.

$C_{10}H_{14}O_5$ (214.2)	Calc.	C	56.1	H	6.6
	Found	»	55.9	»	6.4

*Hydrolysis; identification of propionic acid.* 214 mg of dipropionoxydihydrofuran was boiled for two minutes with 2 ml of *N*/10 sulfuric acid. After cooling the solution was neutralized (methyl red) with *N* sodium hydroxide and a solution of 420 mg of *S*-benzylthiuronium chloride in 2 ml of water was added. A white precipitate was formed at once. The mixture was left for 10 minutes in the ice-box, the precipitate filtered off, washed with 2 ml of ethanol and dried (calcium chloride, 10 mm, 20°, 4 hours). Yield 290 mg of *S*-benzylthiuronium propionate = 61 %. The product was crystallized from ethanol and dried (sulfuric acid, 0.05 mm, 60°, 4 hours). Yield 150 mg = 31 %; m.p. 146–148°; mixed melting point with an authentic specimen of *S*-benzylthiuronium propionate 146–147°; Donleavy<sup>5</sup> found 148°.

$C_{11}H_{16}O_2N_2S$ (240.3)	Calc.	N	11.7
	Found	»	11.5

*Hydrogenation; identification of succinaldehyde.* 3.00 g of dipropionoxydihydrofuran and 15 ml of anhydrous ethanol were shaken with 0.5 g of Raney nickel under 100 atmospheres for 4 hours at room temperature. The reaction product was isolated in the usual way by distillation. Fore-run 0.19 g (b.p.<sub>0.1</sub> = 86–88°); main fraction 2.48 g of dipropionoxytetrahydrofuran = 82 %; b.p.<sub>0.1</sub> = 88–92°;  $n_D^{25} = 1.4378$ . Redistillation gave 2.21 g = 73 %; colourless liquid, b.p.<sub>0.1</sub> = 88–92°;  $n_D^{25} = 1.4375$ .

$C_{10}H_{16}O_5$ (216.2)	Calc.	C	55.5	H	7.5
	Found	»	55.6	»	7.6

It was found that hydrogenation for 8 hours did not change the yield or the quality of the reaction product.

216 mg of dipropionoxytetrahydrofuran was refluxed with 3 ml of *N*/10 sulfuric acid for 15 minutes. After cooling 0.25 ml of phenylhydrazine in 5 ml of *N* acetic acid and 2 ml of ethanol was added. After 1 hour the precipitate of succinaldehyde bis-phenylhydrazone was filtered off, washed thoroughly with water and dried (calcium chloride, 10 mm, 20°, 16 hours); yield 226 mg = 85 %. Yield after crystallization from ethanol and drying (sulfuric acid, 0.1 mm, 50°, 18 hours) 120 mg = 45 %; m.p. 120–122°; Ciamician and Zanetti<sup>6</sup> found 124–125°.

$C_{16}H_{18}N_4$ (266.3)	Calc.	N	21.0
	Found	»	20.9

*Separation into two isomers.* 10.0 g of dipropionoxydihydrofuran, prepared by method 1, was crystallized from 10 ml of anhydrous methanol. The mixture was left at  $-20^{\circ}$  for 1 hour and then at  $-80^{\circ}$  for 30 minutes. The crystals were filtered off (7.6 g, m.p.  $38-47^{\circ}$ ) and the mother liquor distilled in vacuum. Yield 1.8 g of liquid dipropionoxydihydrofuran; b.p.<sub>0.1</sub> =  $88-91^{\circ}$ ;  $n_D^{25} = 1.4522$ .

$C_{10}H_{14}O_5$ (214.2)	Calc.	C	56.1	H	6.6
	Found	»	56.1	»	6.7

The crystalline product (7.6 g) was recrystallized four times from methanol, the melting points being  $46-51^{\circ}$ ,  $55.0-56.5^{\circ}$ ,  $56.0-57.5^{\circ}$  and  $56.0-57.5^{\circ}$ . Yield of final product 3.7 g.

Found	C	56.3	H	6.6
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It was attempted to measure the refractive index of the molten crystals at  $25^{\circ}$ , but the liquid always crystallized before a determination could be made.

*Crystalline isomer; hydrolysis and identification of malealdehyde.* 210 mg of crystalline dipropionoxydihydrofuran was shaken with 1 ml of ethanol and 3 ml of *N*/10 sulfuric acid. The solution became homogenous after 5 hours. After 6 hours 0.25 ml of phenylhydrazine in 10 ml of *N* acetic acid was added and the mixture shaken vigorously. After 1 hour the malealdehyde bis-phenylhydrazone was isolated as above. Yield 92 mg = 35%; m.p.  $171-173^{\circ}$ .

$C_{16}H_{16}N_4$ (264.3)	Calc.	N	21.2
	Found	»	21.0

*Crystalline isomer; hydrogenation.* 1.00 g of crystalline dipropionoxydihydrofuran and 5 ml of anhydrous ethanol were shaken with 0.2 g of Raney nickel under 100 atmospheres for 4 hours and the reaction product isolated as above. Yield 0.78 g of crystalline dipropionoxytetrahydrofuran = 77%; b.p.<sub>0.1</sub> =  $88-91^{\circ}$ ;  $n_D^{25} = 1.4372$ . The product crystallized on cooling to  $-20^{\circ}$ ; m.p.  $11-14^{\circ}$ .

$C_{10}H_{16}O_5$ (216.2)	Calc.	C	55.5	H	7.5
	Found	»	55.8	»	7.5

*Liquid isomer; hydrolysis and identification of malealdehyde.* 212 mg of liquid dipropionoxydihydrofuran was shaken with 1 ml of ethanol and 3 ml of *N*/10 sulfuric acid for 5 hours. The mixture became homogenous after 2 hours. The malealdehyde bis-phenylhydrazone was isolated as above. Yield 106 mg = 41%; m.p.  $171-173^{\circ}$ .

$C_{16}H_{16}N_4$ (264.3)	Calc.	N	21.2
	Found	»	21.3

*Liquid isomer; hydrogenation.* 1.00 g of liquid dipropionoxydihydrofuran was hydrogenated as above. Yield 0.66 g of liquid dipropionoxytetrahydrofuran = 65%; colourless liquid, b.p.<sub>0.1</sub> =  $88-90^{\circ}$ ;  $n_D^{25} = 1.4388$ . The product did not crystallize on standing at  $-20^{\circ}$  for several weeks.

$C_{10}H_{16}O_5$ (216.2)	Calc.	C	55.5	H	7.5
	Found	»	55.6	»	7.4

### 2,5-Dibutyroxy-2,5-dihydrofuran

*Preparation.* 4.5 g of furan (0.066 mole) is added to a solution of 36.5 g of lead tetrabutryrate (0.066 mole) in 135 ml of butyric acid (note 6). The temperature is kept at  $55-60^{\circ}$  for 30 minutes, then at  $65^{\circ}$  for another 30 minutes and finally at  $75-80^{\circ}$  for 45 minutes. The mixture is now a clear pale-yellow solution. The major part of the solvent is distilled under 0.5 mm from a water-bath of  $65-70^{\circ}$  and 250 ml of anhydrous ether is

added to the residue. The mixture is shaken for some minutes and then stirred vigorously whereby the precipitate becomes readily filterable. The lead butyrate is filtered off on a sintered glass disk and washed with anhydrous ether.

The filtrate is evaporated in vacuum from a water-bath of 70° and the residue distilled further in vacuum. After 11 g of a pale-yellow fore-run (b.p.<sub>0.2</sub> < 105°) the main fraction is collected. Yield 12.0 g of dibutyroxydihydrofuran = 75 %; b.p.<sub>0.2</sub> = 104–108°;  $n_D^{25} = 1.4492$ .

11.5 g of the product was redistilled. After 0.5 g of fore-run (b.p.<sub>0.2</sub> < 104°) the main fraction is collected. Yield 10.5 g of a colourless liquid, b.p.<sub>0.2</sub> = 104–107°;  $n_D^{25} = 1.4497$ .

$C_{12}H_{18}O_5$ (242.3)	Calc.	C	59.5	H	7.5
	Found	»	59.2	»	7.5

A sample of dibutyroxydihydrofuran, which was left standing with a little ether at – 20°, crystallized after some months. The main fraction from the above preparation crystallized almost completely at – 20° after inoculation; m.p. – 3 to 1°.

*Hydrolysis; identification of butyric acid.* 484 mg of dibutyroxydihydrofuran was boiled with 4 ml of *N*/10 sulfuric acid until the mixture was homogeneous (10–15 minutes). The *S*-benzylthiuronium salt was then prepared in the usual way. Yield of crude product 790 mg = 78 %. Yield after crystallization from ethanol 350 mg = 35 %; m.p. 146.0–146.5°; mixed m.p. with an authentic specimen of *S*-benzylthiuronium butyrate 146–147°; Donleavy<sup>5</sup> found 146°.

$C_{12}H_{18}O_2N_2S$ (254.3)	Calc.	N	11.0
	Found	»	11.1

*Hydrolysis; identification of malealdehyde.* 205 mg of dibutyroxydihydrofuran was shaken for 22 hours with 1 ml of ethanol and 3 ml of *N*/10 sulfuric acid. 0.25 ml of phenylhydrazine in 10 ml of 3 *N* acetic acid was added and the mixture shaken vigorously. After standing for 1 hour the malealdehyde bis-phenylhydrazone was isolated as above. Yield 62 mg = 28 %; m.p. 171–173°.

$C_{16}H_{16}N_4$ (264.3)	Calc.	N	21.2
	Found	»	21.3

*Hydrogenation; identification of succinaldehyde.* 3.00 g of dibutyroxydihydrofuran and 15 ml of anhydrous ethanol were shaken with 0.2 g of Raney nickel under 100 atmospheres for 4 hours and the reaction product isolated in the usual way. Yield 2.26 g of dibutyroxytetrahydrofuran = 75 %; b.p.<sub>0.1</sub> = 99–104°;  $n_D^{25} = 1.4396$ . Redistillation gave 1.86 g = 62 %; colourless liquid, b.p.<sub>0.1</sub> = 100–104°;  $n_D^{25} = 1.4392$ . The product did not crystallize on standing at – 20° for several weeks.

$C_{12}H_{20}O_5$ (244.3)	Calc.	C	59.0	H	8.3
	Found	»	59.3	»	8.1

It was found that hydrogenation for 8 hours did not change the yield or the quality of the reaction product.

272 mg of dibutyroxytetrahydrofuran was refluxed with 3 ml of *N*/10 sulfuric acid for 30 minutes. After cooling 0.30 ml of phenylhydrazine in 5 ml of *N* acetic acid and 1 ml of ethanol was added and the succinaldehyde bis-phenylhydrazone isolated as above. Yield 240 mg = 80 %. Yield after two crystallizations from ethanol 105 mg = 35 %; m.p. 124–125°.

$C_{16}H_{16}N_4$ (266.3)	Calc.	N	21.0
	Found	»	21.3



## 2,5-Dibenzoxy-2,5-dihydrofuran

*Preparation.* Lead tetrabenzoate is prepared from 135 g of lead tetraacetate (0.30 mole) after Hurd and Austin <sup>7</sup> (cf. also Criegee <sup>8</sup>). This preparation is carried out in a 3-necked round-bottomed flask provided with a stirrer, a thermometer and a reflux condenser with a calcium chloride tube. The flask is placed in a water-bath and the yellow lead tetrabenzoate dissolved in 500 ml of anhydrous benzene. 20.5 g of furan (0.30 mole) is added. The temperature is kept at 50° for 1 hour and then at 75° for 3 hours. At this time the lead tetrabenzoate has disappeared. After cooling the lead benzoate is filtered off on a sintered glass disk and washed with 50 ml of benzene. The solvent is distilled in vacuum from a water-bath of 50°. 51.0 g of crystalline dibenzoxydihydrofuran = 54 % remains.

Dibenzoxydihydrofuran is slightly soluble in ether, methanol and ethanol and somewhat more soluble in acetone and dioxane. When boiled with an aqueous solution of dinitrophenylhydrazine in 2 *N* hydrochloric acid it forms a red precipitate (malealdehyde bis-dinitrophenylhydrazone).

A sample of the above crude product was crystallized from anhydrous methanol and the crystals dried (sulfuric acid, 0.1 mm, 60°, 5 hours); m.p. 165–167° after sintering at 160°.

$C_{18}H_{14}O_5$ (310.3)	Calc. C	69.7	H	4.6
	Found »	69.6	»	4.9

Another sample of the crude product was crystallized from dioxane and dried (sulfuric acid, 0.1 mm, 80°, 18 hours); m.p. 179–182°.

Found C	69.6	H	4.8
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5.84 g of crude product was crystallized 4 times from dioxane, the melting points being 179–182°, 180–182°, 185–189° and 185–189°. All products sintered and turned faintly brown at about 170°. Yield of final product 1.41 g.

Found C	69.6	H	4.7
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*Hydrolysis; identification of benzoic acid.* 310 mg of dibenzoxydihydrofuran (m.p. 185–189°) was refluxed with 3 ml of *N*/10 sulfuric acid and 2 ml of ethanol for 1 1/2 hours. The *S*-benzylthiuronium benzoate was then prepared in the usual way; yield 470 mg = 81 %. Yield after crystallization from ethanol and drying (sulfuric acid, 0.1 mm, 55°, 16 hours) 240 mg = 42 %; m.p. 163–165°; mixed melting point with an authentic specimen of *S*-benzylthiuronium benzoate 163–165°; Donleavy <sup>5</sup> found 166°.

$C_{15}H_{16}O_2N_2S$ (288.4)	Calc. N	9.7
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Found »	9.4
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*Hydrogenation; identification of succinaldehyde.* 2.00 g of dibenzoxydihydrofuran (m.p. 185–189°) in 20 ml of dioxane was shaken with 0.4 g of Raney nickel at 105–115° under 120 atmospheres for 3 hours. After filtration the dioxane was distilled in vacuum. Residue 2.0 g of white crystals. Crystallization from methanol gave 1.17 g of dibenzoxytetrahydrofuran = 58 %; the product melted partly at 80–84° and completely at 125°. Another crystallization from methanol or acetone did not change the melting point. Yield after recrystallization from methanol 0.95 g = 81 %.

$C_{18}H_{16}O_5$ (312.3)	Calc. C	69.2	H	5.2
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Found »	69.2	»	5.2
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350 mg of dibenzoxytetrahydrofuran was refluxed with 2 ml of *N*/10 sulfuric acid and 1 ml of ethanol for 30 minutes. After cooling 0.25 ml of phenylhydrazine in 5 ml of *N* acetic acid was added and the succinaldehyde bis-phenylhydrazone isolated as above;

yield 190 mg = 63 %. Yield after crystallization from ethanol and drying (sulfuric acid, 0.1 mm, 50°, 18 hours) 110 mg = 37 %; m.p. 121–123°.

$C_{16}H_{18}N_4$  (266.3) Calc. N 21.0  
Found N 21.1

Note 1. All materials were technical products.

Note 2. At higher temperatures dark-coloured products are formed.

Note 3. The colour does not disappear on redistillation.

Note 4. Prepared after Criegee<sup>8</sup>. The crude product was used directly without crystallization. It contained propionic acid and the content of lead tetrapropionate was determined iodometrically.

Note 5. The propionic acid and the furan were technical products.

Note 6. The solution of lead tetrabutyrate in anhydrous butyric acid was prepared after Criegee<sup>8</sup>, except that the chlorine treatment was omitted. The content of lead tetrabutyrate was determined iodometrically.

#### SUMMARY

Improved directions are given for the preparation of 2,5-diacetoxy-2,5-dihydrofuran from furan and lead tetraacetate. 2,5-Dipropionoxy-, 2,5-dibutyroxy- and 2,5-dibenzoxy-2,5-dihydrofuran were prepared by a similar reaction. These 2,5-dihydrofurans are new compounds. They were hydrogenated catalytically to the corresponding 2,5-diacyloxytetrahydrofurans, which also are new.

2,5-Diacetoxy-2,5-dihydrofuran and 2,5-dipropionoxy-2,5-dihydrofuran were separated into a liquid and a crystalline isomer, which were shown to be *cis-trans* isomers. Catalytic hydrogenation of the pure isomers gave the corresponding pairs of *cis-trans* isomeric 2,5-diacyloxytetrahydrofurans.

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Received January 9, 1952.