

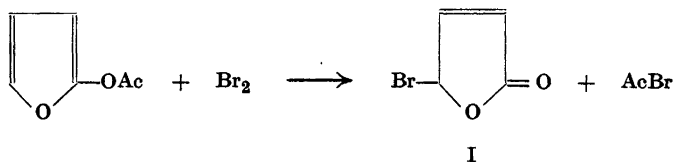
Preparation of Some 5-Substituted 2-Oxo-2,5-dihydrofurans from 2-Acetoxyfuran

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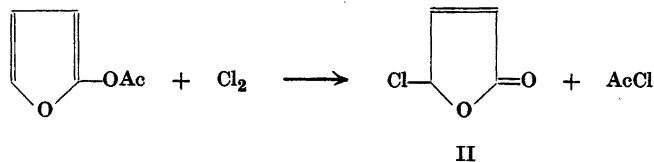
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2-Acetoxyfuran has recently been prepared by pyrolysis of 2,5-diacetoxy-2,5-dihydrofuran¹. We have now investigated the action of certain oxidizing agents on 2-acetoxyfuran.

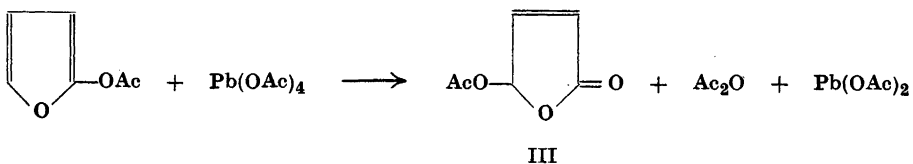
2-Acetoxyfuran reacts with bromine to form 2-oxo-5-bromo-2,5-dihydrofuran I and acetyl bromide. The reaction takes place rapidly at -5 to -10° .



In the same way 2-acetoxyfuran and chlorine gives 2-oxo-5-chloro-2,5-dihydrofuran II and acetyl chloride.

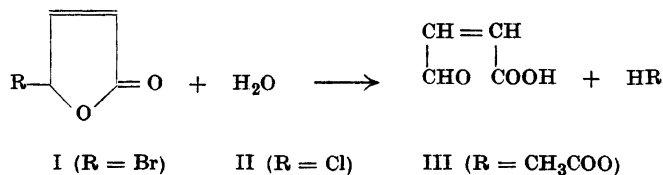


Finally 2-acetoxyfuran and lead tetraacetate in acetic acid at $20-45^{\circ}$ gives 2-oxo-5-acetoxy-2,5-dihydrofuran III.



The similarity of the above reactions suggests that they are of the same type and either all three are electron-sharing reactions or all three are electron-pairing reactions.

The 5-substituted 2-oxo-2,5-dihydrofurans are new compounds. Their structure was proved by hydrolysis to *cis*- β -formylacrylic acid, which was identified as phenylhydrazone.



EXPERIMENTAL

Microanalyses by K. Glens and E. Boss

Reaction of 2-acetoxyfuran with bromine. 5.00 ml of bromine (0.098 mole) in 20 ml of dry carbon tetrachloride was added during 8 minutes to a stirred solution of 12.5 g of 2-acetoxyfuran (0.099 mole) in 20 ml of carbon tetrachloride. The temperature was kept at -5 to -10° . The low boiling products were distilled in vacuum from a water-bath of $30-40^\circ$ and collected in a receiver cooled to -80° . The residue was distilled further in vacuum. Yield 14.7 g of a colourless liquid, which darkens rapidly; b. p.₁₀ = $101-102^\circ$; $n_D^{25} = 1.5343$. Two redistillations, first under 10 mm and then under 0.1 mm, gave a product, which remained colourless. Yield 12.9 g of 2-oxo-5-bromo-2,5-dihydrofuran = 81 %; b. p._{0.1} = $69-70^\circ$, $n_D^{25} = 1.5348$.

$\text{C}_4\text{H}_3\text{O}_2\text{Br}$ (163.0)	Calc.	C 29.5	H 1.9	Br 49.0
	Found	» 29.6	» 2.1	» 48.5

The low boiling products from the above synthesis consist of acetyl bromide and carbon tetrachloride. They were washed into a 100 ml volumetric flask with carbon tetrachloride. 2.00 ml was pipetted out and added to 0.50 ml of aniline in 10 ml of anhydrous ether. A white precipitate, which was formed immediately, was filtered off and washed with ether; yield 300 mg of aniline hydrobromide = 88 %. Dissolution in ethanol and precipitation with ether gave 260 mg = 76 %.

$\text{C}_6\text{H}_5\text{NBr}$ (174.1)	Calc.	N 8.0	Br 45.9
	Found	» 7.8	» 46.4

The filtrate from the aniline hydrobromide was evaporated in vacuum and the residue crystallized from 10 ml of water and then from 5 ml of ethanol. Yield 90 mg of acetanilide = 34 %; m. p. $113-114^\circ$ (Hershberg apparatus, corr.).

$\text{C}_8\text{H}_9\text{ON}$ (135.2)	Calc.	N 10.4
	Found	» 10.5

Hydrolysis of 2-oxo-5-bromo-2,5-dihydrofuran. 190 mg of 2-oxo-5-bromo-2,5-dihydrofuran was boiled with 2 ml of water for a few seconds. 0.6 ml of phenylhydrazine in 2 ml of glacial acetic acid and 5 ml of water was added. The yellow precipitate was filtered off after 10 minutes, washed with water and dried. Yield 180 mg of *cis*- β -formylacrylic acid

phenylhydrazone = 81 %. Crystallization from acetone-benzene gave 105 mg = 47 %; m. p. 147–148° (compare Schenck and Appel² and Hellström³).

$C_{10}H_{10}N_2O_2$ (190.2)	Calc.	C 63.2	H 5.3	N 14.7
	Found	» 63.5	» 5.2	» 14.5

Reaction of 2-acetoxyfuran with chlorine. 2.35 ml of chlorine (measured at -80°) (0.055 mole) was evaporated into 6.7 g of 2-acetoxyfuran (0.053 mole) in 10 ml of carbon tetrachloride at -40 to -50° during 10 minutes. Towards the end of the chlorination, the reaction mixture turned yellow. The mixture was heated to room temperature and left standing for 10 minutes. The reaction products were isolated as above.

Yield 4.81 g of 2-oxo-5-chloro-2,5-dihydrofuran = 77 %; colourless liquid; b. p.₁₃ = 91–95°; n_D^{25} = 1.4884. Two redistillations gave 3.33 g = 53 %; b. p.₁₄ = 91–93°; n_D^{25} = 1.4884.

$C_4H_3O_2Cl$ (118.5)	Calc.	C 40.5	H 2.6	Cl 29.9
	Found	» 40.1	» 2.8	» 31.0

It is apparent from the analytical evidence, that the product contains a certain amount of a chloro-compound with more chlorine and less carbon than 2-oxo-5-chloro-2,5-dihydrofuran.

Yield of reprecipitated aniline hydrochloride 91 mg = 66 %.

C_6H_8NCl (129.6)	Calc.	N 11.0	Cl 27.4
	Found	» 10.8	» 27.9

Yield of crystallized acetanilide 21 mg = 15 %; m. p. 112–114°.

Found	N	10.4
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Hydrolysis of 2-oxo-5-chloro-2,5-dihydrofuran. *Cis-β*-formylacrylic acid phenylhydrazone was prepared from 140 mg of 2-oxo-5-chloro-2,5-dihydrofuran as above. Yield of crude product 150 mg = 67 %. Yield after crystallization 80 mg = 36 %; m. p. 148–150°.

Found	C	63.6	H	5.4	N	14.3
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Reaction of 2-acetoxyfuran with lead tetraacetate. A suspension of lead tetraacetate was prepared in the usual way⁴ from 55.0 g of red lead oxide (0.080 mole), 105 ml of glacial acetic acid and 41 ml of acetic anhydride. 10.1 g of 2-acetoxyfuran (0.080 mole) was added at once with stirring and the temperature kept at 20–25° for 30 minutes by external cooling and then raised to 40° and kept at 40–45° for 30 minutes. The reaction product was isolated as described previously for the preparation of 2,5-diacetoxy-2,5-dihydrofuran⁵. Yield 10.0 g of 2-oxo-5-acetoxy-2,5-dihydrofuran = 88 %; b. p._{0.2} = 85–88°; n_D^{25} = 1.4593. The product was an almost colourless liquid. Redistillation gave 8.9 g; b. p._{0.05} = 72–73°; n_D^{25} = 1.4594.

$C_4H_3O_3(CH_3CO)$ (142.1)	Calc.	C 50.7	H 4.3	CH_3CO 30.3
	Found	» 50.9	» 4.1	» 30.2

Hydrolysis of 2-oxo-5-acetoxy-2,5-dihydrofuran. *Cis-β*-formylacrylic acid phenylhydrazone was prepared from 340 mg of 2-oxo-5-acetoxy-2,5-dihydrofuran as above, except that the preliminary hydrolysis was carried out by boiling with 5 ml of *N*/10 sulfuric acid for 4 minutes. Yield of crude product 295 mg = 65 %. Yield after two crystallizations 130 mg = 29 %; m. p. 147–148°.

Found	C	63.2	H	5.5	N	14.6
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SUMMARY

2-Acetoxyfuran has been found to react (1) with bromine to give 2-oxo-5-bromo-2,5-dihydrofuran and acetyl bromide, (2) with chlorine to give 2-oxo-5-chloro-2,5-dihydrofuran and acetyl chloride, and (3) with lead tetraacetate to give 2-oxo-5-acetoxy-2,5-dihydrofuran. The dihydrofurans are all new compounds. They could be hydrolyzed to *cis*- β -formylacrylic acid.

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