

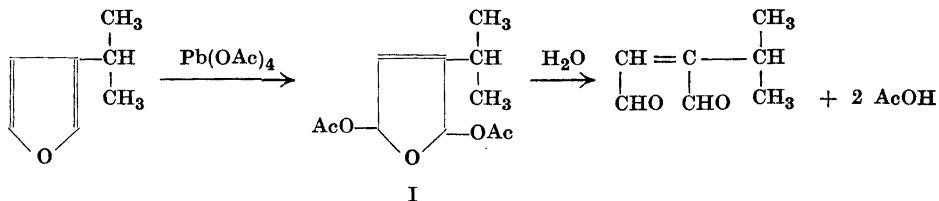
## The Acetoxylation of Furans with Lead Tetraacetate; Preparation of 2,5-Diacetoxy-3-isopropyl-2,5-dihydrofuran

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It has been found previously by Clauson-Kaas<sup>1</sup>, that furan can be acetoxy-  
lated with lead tetraacetate to 2,5-diacetoxy-2,5-dihydrofuran. Later Clauson-  
Kaas, Limborg and Fakstorp<sup>2</sup> failed to acetoxy-  
late furoic acid and ethyl  
furoate by this method. The acetoxylation with lead tetraacetate of some other  
 $\alpha$ -substituted furans, *viz.* silvan, furfuryl acetate, furfural diacetate and 2-ace-  
tylfuran, has now been attempted but also without success, as no pure com-  
pounds could be isolated.

$\beta$ -Isopropylfuran was, contrary to the  $\alpha$ -substituted furans, acetoxy-  
lated by lead tetraacetate. The reaction was somewhat more rapid than the reac-  
tion between furan and lead tetraacetate. The resulting diacetoxy-isopropyl-  
dihydrofuran gave — after hydrolysis and addition of dinitrophenylhydrazine  
to the hydrolysate — a dinitrophenylhydrazone with the formula  $C_{13}H_{14}O_5N_4$ ,  
which was identical with the hydrazone of isopropylmalealdehyde prepared  
previously from a hydrolysate of 2,5-dimethoxy-3-isopropyl-2,5-dihydrofuran<sup>3</sup>.  
This reaction proves that the new compound is 2,5-diacetoxy-3-isopropyl-2,5-  
dihydrofuran I.



### EXPERIMENTAL

Microanalyses by Franz Limborg and Kirsten Glens

*Attempts to acetoxy-  
late some  $\alpha$ -substituted furans.* The action of lead tetraacetate on  
silvan, furfuryl acetate, furfural diacetate and 2-acetylfuran was investigated. The

procedure described previously<sup>4</sup> for the acetoxylation of furan was employed. The progress of the reaction was followed by adding samples of the reaction mixture to water. When the lead tetraacetate had disappeared the reaction mixture was a clear, homogeneous yellow or light-brown solution. In spite of several attempts at different reaction temperatures it was in no case found possible to isolate any pure reaction products.

*2,5-Diacetoxy-3-isopropyl-2,5-dihydrofuran (I)*. 4.4 g of  $\beta$ -isopropylfuran<sup>5</sup> (0.040 mole) was added to a suspension of 17.7 g of lead tetraacetate (0.040 mole) in 100 ml of glacial acetic acid. The mixture was kept at 55–60° for 35 minutes and the reaction product isolated in the usual way<sup>4</sup>. The final distillation gave a fore-run of 0.6 g (b. p.<sub>0.1</sub> = 65–82°) and 4.9 g of crude diacetoxy-isopropyl-dihydrofuran = 54 %; b. p.<sub>0.1</sub> = 84–90°;  $n_D^{25}$  = 1.4550.

4.6 g of the crude product was redistilled. After a fore-run of 0.7 g (b. p.<sub>0.1</sub> = 84–88°,  $n_D^{25}$  = 1.4547) the main fraction was collected; yield 3.3 g of a pale-yellow liquid; b. p.<sub>0.1</sub> = 88–91°;  $n_D^{25}$  = 1.4550.

$C_7H_{10}O_3(CH_3CO)_2$ (228.2)	Calc.	C 57.9	H 7.1	$CH_3CO$ 37.7
	Found	» 58.3	» 7.0	» 36.3

*Mono-dinitrophenylhydrazone of isopropylmalealdehyde*. 57 mg of 2,5-diacetoxy-3-isopropyl-2,5-dihydrofuran was boiled with 2 ml of *N*/10 sulfuric acid for one minute. After cooling 50 ml of an 0.2 % solution of dinitrophenylhydrazine in 2 *N* hydrochloric acid was added, the mixture shaken vigorously and then left standing for 1.5 hours with occasional shaking. The orange-red precipitate was filtered off, washed thoroughly with water and dried. Yield 50 mg of isopropylmalealdehyde dinitrophenylhydrazone = 66 %. Crystallization from absolute ethanol gave 25 mg = 33 %; m. p. 175–177° (Hershberg apparatus, corr.); mixed melting point with the dinitrophenylhydrazone prepared from dimethoxy-isopropyl-dihydrofuran<sup>3</sup> 174–176°.

$C_{13}H_{14}O_5N_4$ (306.3)	Calc.	C 51.0	H 4.6	N 18.3	$CH_3CO$ 0
	Found	» 50.8	» 4.6	» 17.9	» 0.3

#### SUMMARY

Attempts to acetoxylate silvan, furfuryl acetate, furfural diacetate and 2-acetylfuran with lead tetraacetate were unsuccessful.  $\beta$ -Isopropylfuran and lead tetraacetate gave the new 2,5-diacetoxy-3-isopropyl-2,5-dihydrofuran.

#### REFERENCES

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Received January 29, 1952.