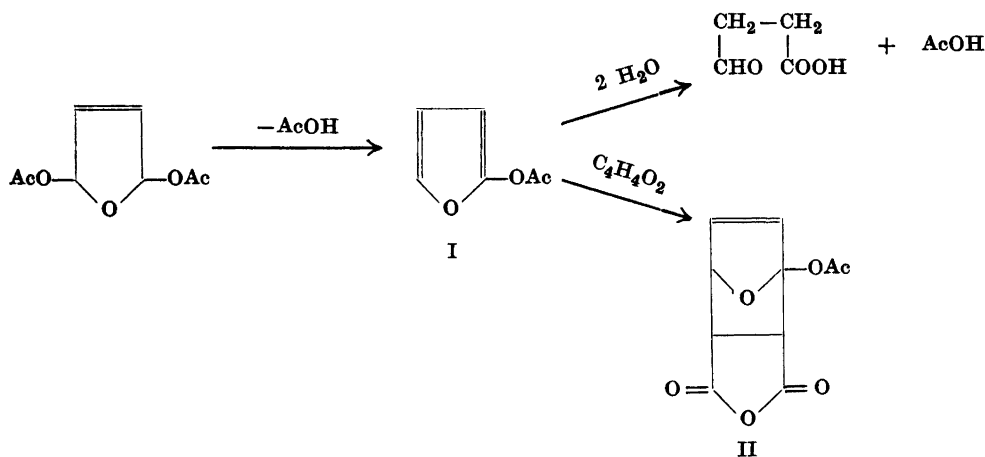


2-Acetoxyfuran

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We have found that by pyrolysis of 2,5-diacetoxy-2,5-dihydrofuran a colourless liquid compound with the formula $C_4H_3O_2(COCH_3)$ is formed¹. This compound reacts (1) with dinitrophenylhydrazine in 2 *N* aqueous hydrochloric acid to give the dinitrophenylhydrazone of β -formylpropionic acid; (2) with phenylhydrazine to give the hydrazone-hydrazone of β -formylpropionic acid and (3) with maleic anhydride to form an addition product. The compound must therefore be the hitherto unknown 2-acetoxyfuran I while the addition product probably has the structure II.

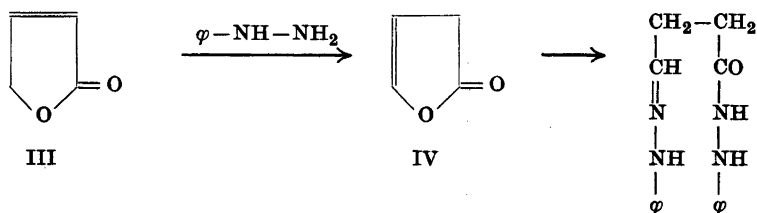


The course of the pyrolysis of diacetoxydihydrofuran depends upon its quality. Diacetoxydihydrofuran, prepared from furan and lead tetraacetate², gives a 35 per cent yield of 2-acetoxyfuran. If the diacetoxydihydrofuran is first roughly separated into the crystalline and the liquid isomer², and these pyrolyzed separately, the crystalline isomer gives 24 per cent of 2-acetoxyfuran,

while the liquid isomer gives 40 per cent. These results are consistent with our earlier findings² in that diacetoxydihydrofuran, prepared by the lead salt method, consists of about 1/3 of the crystalline and 2/3 of the liquid isomer.

Pyrolysis of diacetoxydihydrofuran, prepared by the bromine method³, can also give about 35 per cent of 2-acetoxyfuran. But the yield is often considerably lower and at the same time varying amounts of γ -hydroxycrotonolactone (III) are formed. One experiment gave for instance 7 per cent of 2-acetoxyfuran and 19 per cent of γ -hydroxycrotonolactone. We believe that the variable behaviour of diacetoxydihydrofuran prepared by the bromine method, in the pyrolytic reaction, is due to the formation of small amounts of hydrogen bromide during the reaction^{cf. 3}. Probably γ -hydroxycrotonolactone is formed from 2-acetoxyfuran and not directly from diacetoxydihydrofuran.

γ -Hydroxycrotonolactone gives no precipitate with dinitrophenylhydrazine in hydrochloric acid but, like 2-acetoxyfuran, gives the phenylhydrazone-hydrazone of β -formylpropionic acid by reaction with phenylhydrazine. This has previously been found by Glattfeld *et al.*⁴, who, however, were unable to identify their product. Evidently γ -hydroxycrotonolactone is first transformed by phenylhydrazine into 2-oxo-2,3-dihydrofuran IV or its equivalent, which then reacts further to give the hydrazone-hydrazone. This is in agreement with what is known in general about the behaviour of α , β -unsaturated lactones (*cf.* Paist, Blout, Uhle and Elderfield⁵).



EXPERIMENTAL

Microanalyses by K. Glens and E. Boss

Pyrolysis of 2,5-diacetoxy-2,5-dihydrofuran. (1). 50.0 g of diacetoxydihydrofuran, prepared from furan and lead tetraacetate¹, was pyrolyzed under 10 mm in an apparatus of the Bouveault type⁶ (Fig. 1).

The temperature of the oven was kept at 480–500°. The diacetoxydihydrofuran was kept boiling at such a rate that the temperature at the top of the condenser remained at 65–70°. The colour of the content of the distilling flask changed from pale-yellow to dark-brown during the reaction. After about 2 hours the reaction was stopped. 8 g of a black pitchy mass remained in the distilling flask. The cooling-trap contained 38 g of

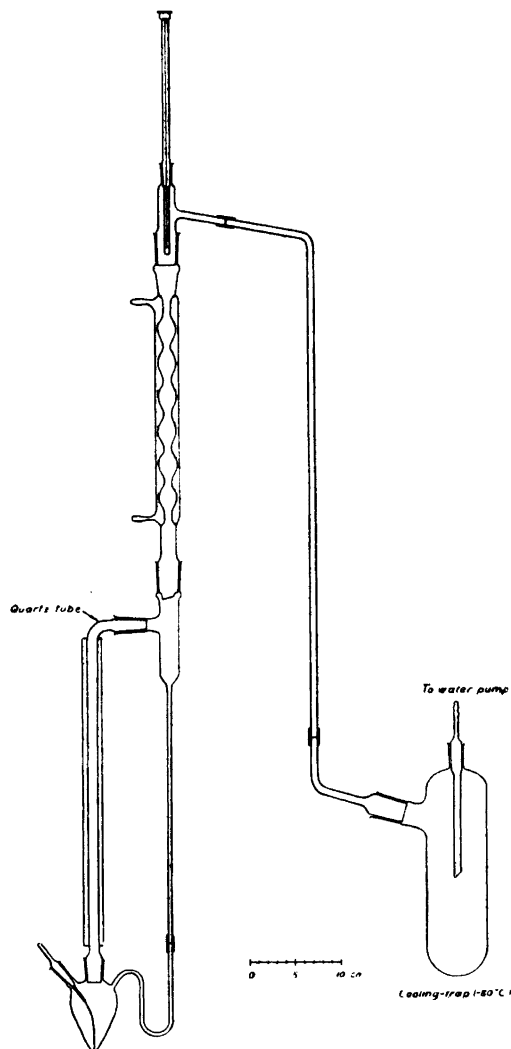


Fig. 1.

a partially crystalline product, which melted at room temperature to a pale-yellow liquid. Distillation under 15 mm through a short column gave 29 g of distillate, b. p.₁₅ < 65°. Further distillation of the residue without the column gave 5.10 g of regenerated diacetoxydihydrofuran = 10 %; b. p.₉ = 125–130°; n_D^{25} = 1.4544. The product crystallized partly at room temperature after inoculation *Cf.* 2.

The distillate (29 g) was dissolved in 50 ml of ether and washed with 75 ml of water and then 4 times with 25 ml of 2 *M* potassium hydrogen carbonate. Drying and distillation of the ethereal solution gave 12.0 g of 2-acetoxyfuran = 35 %; colourless liquid, b. p.₉ =

49–50°; $n_D^{25} = 1.4480$; the UV-spectrum in 96 % ethanol showed a flat maximum at 212 $m\mu$; $\log \epsilon_{\max} = 3.72$.

$C_4H_3O_2(COCH_3)$ (126.1)	Calc.	C 57.1	H 4.8	COCH ₃ 34.1
	Found	» 57.2	» 4.8	» 33.6

2-Acetoxyfuran, like furan itself, turns yellow on standing, probably due to autoxidation. By addition of ether to an old sample of 2-acetoxyfuran, a white amorphous substance separates.

(2). Diacetoxydihydrofuran, prepared from furan and lead tetraacetate, was separated roughly by decantation into the crystalline and the liquid isomer. Pyrolysis of the crystalline isomer as above gave 24 %, while pyrolysis of the liquid isomer gave 40 % of 2-acetoxyfuran.

(3). 50.0 g of diacetoxydihydrofuran, prepared by the bromine method³, was pyrolyzed as above (reaction time 1.5 hours). Yield 12.5 g of 2-acetoxyfuran = 37 %; b. p.₁₄ = 54–55°; $n_D^{25} = 1.4480$.

(4). Three 50 g-portions of another sample of diacetoxydihydrofuran, also prepared by the bromine method, gave by pyrolysis 114 g of liquid in the cooling-trap. Distillation through a short column gave first 84 g with b. p.₁₅ < 65°, from which 7 g of 2-acetoxyfuran = 7 % was isolated as above; b. p.₁₃ = 53–54°; $n_D^{25} = 1.4479$. Further distillation gave 13 g of a pale-yellow liquid; b. p.₁₃ = 95–98°; $n_D^{25} = 1.4665$. Redistillation after 2 months through a short column gave 10 g of a colourless liquid; b. p.₁₃ = 100–102°; $n_D^{25} = 1.4660$. 5.0 g of this product was crystallized rapidly from 5 ml of ether and distilled. Yield 2.1 g; b. p.₁₂ = 88–89°; m. p. 4–5°; $n_D^{25} = 1.4662$; previously found for γ -hydroxycrotonolactone b. p.₁₂ = 92–93°⁷, m. p. 5.0–5.3°⁸.

$C_4H_4O_2$ (84.1)	Calc.	C 57.1	H 4.8	COCH ₃ 0
	Found	» 57.1	» 4.8	» 0

The yield of γ -hydroxycrotonolactone (13 g) corresponds to 19 % of the theoretical amount. The crystallized sample gave no precipitate with dinitrophenylhydrazine in 2 N hydrochloric acid.

Reaction of 2-acetoxyfuran and γ -hydroxycrotonolactone with phenylhydrazine. 126 mg of 2-acetoxyfuran and 0.30 ml of phenylhydrazine were mixed and heated to 100° for 3 hours. After cooling the reaction mixture was washed 4 times with ether and the remaining crystals crystallized from ethanol. Yield 120 mg of β -formylpropionic acid phenylhydrazone-hydrazone = 43 %; m. p. 181–182° (Hershberg apparatus, corr.); previously found⁹ 182°.

$C_{16}H_{18}ON_4$ (282.3)	Calc.	C 68.1	H 6.4	N 19.9
	Found	» 68.1	» 6.6	» 19.9

β -Formylpropionic acid phenylhydrazone-hydrazone was prepared from 84 mg of γ -hydroxycrotonolactone and 0.30 ml of phenylhydrazine as above. Yield 100 mg = 36 %; m. p. 182–183°; mixed melting point with a sample prepared from 2-acetoxyfuran 180–182°.

Found	C 68.1	H 6.5	N 20.0
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Reaction of 2-acetoxyfuran with dinitrophenylhydrazine in 2 N hydrochloric acid. A few drops of 2-acetoxyfuran were added to an 0.2 % solution of dinitrophenylhydrazine in 2 N hydrochloric acid and the resulting dinitrophenylhydrazone of β -formylpropionic acid isolated in the usual way and crystallized from dioxane-petroleum ether; m. p. 197–203°; previously found¹⁰ 198–200°.

$C_{10}H_{10}O_6N_4$ (282.2)	Calc.	C 42.6	H 3.6	N 19.9
	Found	» 42.3	» 4.0	» 19.7

Reaction of 2-acetoxymfuran with maleic anhydride. 0.63 g of 2-acetoxymfuran (0.005 mole) and 0.50 g of maleic anhydride (0.005 mole) were dissolved in 5 ml of benzene and the solution evaporated to 1–2 ml. On cooling the reaction mixture solidified to a mass of white crystals, which were washed 4 times with benzene. Yield 0.75 g of addition product = 67 %; m. p. 132–133°. Crystallization from benzene did not change the melting point.

$C_8H_5O_5(COCH_3)$ (224.2)	Calc.	C	53.6	H	3.6	COCH ₃	19.2
	Found	»	54.0	»	3.9	»	18.9

SUMMARY

2-Acetoxymfuran, which is a new compound, has been prepared by pyrolysis of 2,5-diacetoxy-2,5-dihydrofuran. Pyrolysis of certain impure samples of diacetoxydihydrofuran gave varying amounts of 2-acetoxymfuran together with γ -hydroxycrotonolactone.

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