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

NIELS ELMING

Centrallaboratoriet, Sadolin & Holmblad A/S, Copenhagen, Denmark

It has been found previously by Clauson-Kaas, that furan can be acetoxylated with lead tetraacetate to 2,5-diacetoxy-2,5-dihydrofuran. Later Clauson-Kaas, Limborg and Fakstorp failed to acetoxylate furoic acid and ethyl furoate by this method. The acetoxylation with lead tetraacetate of some other α-substituted furans, viz. silvan, furfuryl acetate, furfural diacetate and 2-acetylfuran, has now been attempted but also without success, as no pure compounds could be isolated.

β-Isopropylfuran was, contrary to the α-substituted furans, acetoxylated by lead tetraacetate. The reaction was somewhat more rapid than the reaction 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_{18}H_{14}O_{5}N_{4}, which was identical with the hydrazone of isopropylmaledehyde prepared previously from a hydrolysate of 2,5-dimethoxy-3-isopropyl-2,5-dihydrofuran. This reaction proves that the new compound is 2,5-diacetoxy-3-isopropyl-2,5-dihydrofuran I.

![Chemical structure of compound I](image)

EXPERIMENTAL

Microanalyses by Franz Limborg and Kirsten Glens

Attempts to acetoxylate some α-substituted furans. The action of lead tetraacetate on silvan, furfuryl acetate, furfural diacetate and 2-acetylfuran was investigated. The
procedure described previously 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 β-isopropylfur'an (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. The final distillation gave a fore-run of 0.8 g (b. p.0.1 = 65—82°) and 4.9 g of crude diacetoxy-isopropyl-dihydrofuran = 54 %; b. p.0.1 = 84—90°; nD = 1.4550. 4.6 g of the crude product was redistilled. After a fore-run of 0.7 g (b. p.0.1 = 84—88°, nD = 1.4547) the main fraction was collected; yield 3.3 g of a pale-yellow liquid; b. p.0.1 = 88—91°; nD = 1.4550.

C7H10O2(CH3CO)2 (228.2) Cal. C 57.9 H 7.1 CH3CO 37.7
Found → 58.3 → 7.0 → 36.3

Mono-dinitrophenyldiazone 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 dinitrophenyldiazone = 66 %. Crystallization from absolute ethanol gave 25 mg = 33 %; m. p. 175—177° (Hershberg apparatus, corr.); mixed melting point with the dinitrophenyldiazone prepared from dimethoxy-isopropyl-dihydrofuran 3 174—176°.

C13H14O5N4 (306.3) Cal. C 51.0 H 4.6 N 18.3 CH3CO 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. β-Isopropylfur'an and lead tetraacetate gave the new 2,5-diacetoxy-3-isopropyl-2,5-dihydrofuran.

REFERENCES


Received January 29, 1952.