

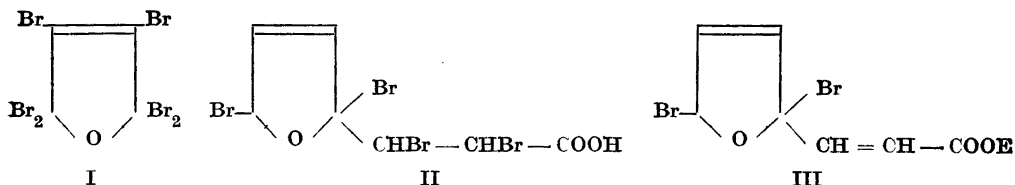
The Action of Bromine on Furans

A New Synthesis of 2,5-Diacetoxy-2,5-dihydrofuran

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The reaction between bromine and simple furans is believed to be initiated by a 1,4-addition of bromine to the double bonds of the furan nucleus¹, thus yielding a 2,5-dibromo-2,5-dihydrofuran. However, so far only three such preliminarily formed addition compounds have actually been isolated and analyzed. Hill and Hartshorn² obtained a hexabromo-dihydrofuran from the interaction of tetrabromofuran and bromine. Moureu, Dufraisse and Johnson³ prepared a tetrabromo addition compound of furylacrylic acid by the action of a solution of bromine in chloroform at -15° ; and Gilman and Wright⁴ isolated a dibromo addition product of ethyl furylacrylate by a similar synthesis. In consistency with the conception of 1,4-addition the formulas I—III are to be ascribed to these substances.

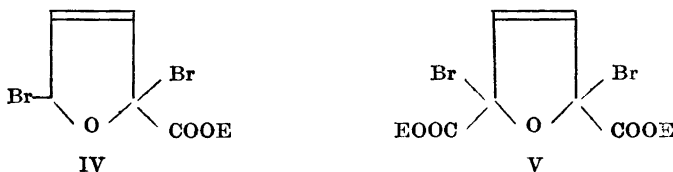


Hill and Hartshorn did not propose any formula for their compound, but formula I is in agreement with the fact, that the bromide was hydrolyzed by water to dibromomaleic acid.

Moureu, Dufraisse, and Johnson suggested that a 1,1-addition of bromine to the oxygen of the furan nucleus had taken place, but in view of the discussion given earlier, this is not likely (see Clauson-Kaas¹).

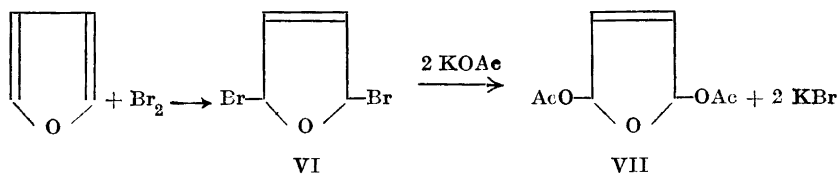
Gilman and Wright took no final decision as to the formula of their dibromo ester, but are inclined to formula III.

The formation of a dibromo compound of ethyl furoate has been claimed by Schiff and Tassinari ⁵, but the existence of this substance was later questioned by Hill and Sanger ⁶. Yet it is not impossible, that Schiff and Tassinari's substance actually has been ethyl 2,5-dibromo-2,5-dihydrofuroate (IV). In this connection it should be mentioned, that the oil obtained by Klinkhardt ⁷ when treating 2,5-dicarbethoxyfuran with bromine might have a similar structure (V). Still neither of these addition products were analyzed or subjected to a closer study.



The above experiments have not been repeated here; but the action of bromine on furan itself has been investigated and proof of the formation of a 1,4-addition compound, namely 2,5-dibromo-2,5-dihydrofuran, is given.

It was to be expected, that 2,5-dibromo-2,5-dihydrofuran (VI) would be very unstable and no attempt was made to isolate it in a pure state. From earlier experiments on the alkoxylation of furan with methanolic bromine ¹ there was some reason to believe that the bromine atoms of dibromodihydrofuran might be sufficiently active to react with metal salts of organic acids to yield acyloxy compounds and metal bromide. Therefore the bromination of furan was undertaken in a solution of acetic acid containing two moles of potassium acetate. In fact the reaction took the expected course and 2,5-diacetoxy-2,5-dihydrofuran (VII) was obtained in a good yield.



This synthesis proves that the initial reaction between furan and bromine is a 1,4-addition of bromine to the double bonds of the furan nucleus.

The diacetoxydihydrofuran has earlier been prepared by the action of lead tetraacetate on furan ¹ and the identity of the two products was easily established by comparison of the physical properties and by identification of the malealdehyde formed by hydrolysis.

EXPERIMENTAL

20 g of anhydrous potassium acetate (0.2 mole) and 7.25 ml of freshly distilled furan (0.1 mole) are dissolved in 100 ml of perfectly dry acetic acid and the mixture cooled to 10°. A solution of 5 ml of bromine (0.1 mole) in 100 ml of acetic acid is added under efficient stirring during 5—10 minutes. The temperature is kept at 10°. The potassium bromide formed by the reaction is filtered off by suction and the filtrate evaporated in vacuum. When the distillation of acetic acid has ceased, 100 ml of ether is added to the residue. A small precipitate of potassium bromide and potassium acetate is filtered off and washed with ether. The total ether fraction is evaporated on the water bath at ordinary pressure and the residue distilled in vacuum. There is a small fore-run of acetic acid, then the diacetoxy compound distills at 129—132°/9 mm as a perfectly colourless, very viscous oil (previously found¹ 128—129°/10 mm). Towards the end of the distillation the temperature is allowed to rise to 140°. Yield 13 g = 70 %.

$C_8H_{10}O_5$ (186)	Calc. C 51.60	H 5.42
	Found C 51.31	H 5.34

Hydrolysis and identification of malealdehyde as bis-phenylhydrazone was performed as described earlier¹. Yield of crude product 72 %. Yield after recrystallization 62 %. M. p. 170—172° (Kofler stage, corr. Clauson-Kaas and Fakstorp⁸ 171°).

$C_{16}H_{16}N_4$ (264)	Calc. N 21.21	Found N 21.32
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SUMMARY

The action of bromine on the furan nucleus is discussed and the conception of an initial 1,4-addition is confirmed by the synthesis of 2,5-diacetoxy-2,5-dihydrofuran from furan and bromine in a solution of acetic acid containing potassium acetate.

The analyses have been performed in the most careful way by my colleague Mr. O. Rosenlund Hansen.

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