

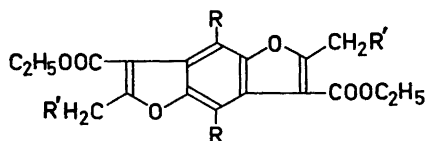
Bromination and Subsequent Ozonisation of Ethyl 2,6-Dimethylbenzo [1.2-b, 4.5-b'] difuran-3,7-dicarboxylate

ERLING BERNATEK, TORE LEDAAL and
SIGURD STEINSVIK

*Universitetets Kjemiske Institutt,
Blindern - Oslo, Norway*

Ethyl 2,6-dimethylbenzo[1.2-b, 4.5-b'] difuran-3,7-dicarboxylate I was chlorinated by Ikuta in 1892¹ and chlorine was found to attack the 4- and 8- position giving a dichloro compound II.

Ikuta found an independent synthesis of II through the reaction between chloranil and sodium acetoacetic ester. Two keto-ester groups were thus introduced in the quinone while subsequent reduction and ring-closure afforded II.



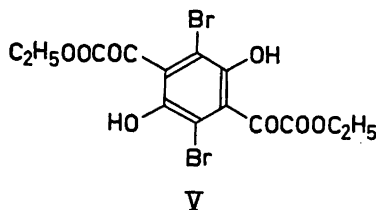
- I R=R'=H
 II R=Cl, R'=H
 III R=Br, R'=H
 IV R=R'=Br

Some years ago it was found² that compound I was able to form a very stable monozonide and an even more stable diozonide, and the interest for this class of compounds was thus to some extent revived.

We wish to report some experiments on the bromination of I and ozonisation of the brominated products. I was dissolved in chloroform and bromine added at room temperature in the presence of an iron bromide catalyst. One mole of bromine was absorbed and the dibromo compound III could be isolated in quantitative yield. If the bromine was added to the solution in absence of a catalyst and the reaction mixture irradiated with ultraviolet light, two moles of bromine was consumed and a tetrabromo compound IV was quantitatively formed. It could be transformed into

III by reduction with zinc dust in glacial acetic acid.

On ozonisation in ethyl acetate III gave a diozonide C₁₈H₁₆O₁₂Br₂ which possessed a considerable stability. It could not be rearranged³ by treatment with acetic anhydride and concentrated sulphuric acid. A probable monozonide could also be isolated. Reduction of the diozonide with sodium iodide in glacial acetic acid afforded a compound C₁₄H₁₂O₈Br₂ which evidently contained carbonyl and free hydroxyl groups. Most probably it has the structure V where the two expected acetyl groups have been lost during the working-up procedure. V could easily be acetylated to a diacetyl derivative, C₁₈H₁₆O₁₀Br₂.



The tetrabromo compound IV also gave a stable diozonide, which proves that the additional two bromine atoms have not been added to any of the furan double bonds. On reduction with sodium iodide as before a compound C₁₄H₁₂O₈Br₂ was again isolated, which was found to be identical with V. It seems therefore likely that the tetrabromo compound has the proposed structure IV, where two bromine atoms sit in the aromatic nucleus while the other two are in the methyl groups. Also from IV a probable monozonide could be isolated.

Ikuta mentions that the dichloro compound II can form an oily "addition compound" with chlorine from which it can be regenerated by the action of zinc in glacial acetic acid, but he gives no analytical data. Also II has now been found to form a diozonide C₁₈H₁₆O₁₂Cl₂, which could not be rearranged by the usual method and which, by reduction with sodium iodide gave a product C₁₄H₁₂O₈Cl₂ probably analogous to V.

Experimental. Dibromo derivative III. I (5 g) was dissolved in chloroform (150 ml), some iron wool was added and bromine (40 g) added dropwise during 8 h. The mixture was kept at room temperature for 24 h whereafter it was washed with aqueous sodium bisulphite to remove unreacted bromine and with water.

After drying and evaporation of the chloroform fine crystals were left (7.5 g), (contained evidently a small amount of IV). Recrystallised from glacial acetic acid, m.p. 165°C. (Found: C 44.4; H 3.5; Br 32.4. Calc. for $C_{18}H_{16}O_6Br_2$: C 44.3; H 3.3; Br 32.7.)

Tetrabromo derivative IV. I (4 g) was dissolved in chloroform (150 ml) and bromine (60 g) added dropwise during 8 h. The mixture was kept for a total of 24 h and irradiated with ultraviolet light all the time. It was reduced to a volume of ca. 100 ml *in vacuo* and thereafter washed with aqueous sodium bisulphite, dried and evaporated. White needles remained (8 g), recrystallised from acetic acid the substance had m.p. 195°C. (Found: C 33.6; H 2.2; Br 49.8. Calc. for $C_{18}H_{14}O_6Br_4$: C 33.5; H 2.2; Br 49.5.)

Reduction of IV. Tetrabromo derivative (3 g) in glacial acetic acid (50 ml) was reduced with zinc dust at 30°C for 5 h with occasional shaking. The mixture was diluted with cold water (300 ml) and the separated substance collected and washed thoroughly. Dried and extracted at room temperature with ethyl acetate. Evaporation of the solvent gave white needles. M.p. alone and in mixture with III 166°C.

Ozonide of dibromo derivative. III (4.0 g) was dissolved in ethyl acetate (150 ml) and ozone (4 % in oxygen) was passed into the solution in about 10 % excess of the amount required for the formation of a dioxonide. The ethyl acetate was evaporated and the remaining crystals washed with a small amount of ethanol and became then white (3.6 g). Recrystallised from dilute ethanol. M.p. 145°C. (Found: C 37.4; H 2.8; Br 27.4; act. O 5.5. Calc. for $C_{18}H_{16}O_{12}Br_2$: C 37.0; H 2.8; Br 27.4; act. O 5.5.) The ethanol used for washing the crude ozonide was concentrated and yellow crystals separated (0.5 g). These were extracted at room temperature with ethanol-water (3:1) and the extract slowly concentrated. Large yellow crystals were formed. M.p. ca. 90°C. (Found: Act. O 3.3. Calc. for $C_{18}H_{16}O_6Br_2$: Act. O 3.2.)

Reduction of the dioxonide. The ozonide (3.5 g) was dissolved in chloroform (100 ml) and the solution cooled to -20°C. Twice the calculated amount of sodium iodide was dissolved in glacial acetic acid and the two solutions mixed. After about 1 h the liberated iodine was removed with aqueous sodium bisulphite and the acetic acid with sodium bicarbonate. After washing and drying the chloroform was evaporated. A dark viscous oil remained, which crystallised partly after several days in a vacuum desiccator. The crystals were washed with cold petrol ether and recrystallised from a mixture of petrol ether and benzene. Yellow

needles m.p. 132°C. (Found: C 35.6; H 2.6; Br 35.1. Calc. for $C_{14}H_{12}O_8Br_2$: C 35.9; H 2.6; Br 34.2.) The substance gave a precipitate with 2,4-dinitrophenylhydrazine and a yellowish brown colour with ferric chloride. It dissolved easily in aqueous sodium hydroxide with a red colour. Acetylation was effected by dissolving it (1 g) in acetic anhydride (10 ml) to which anhydrous sodium acetate (1 g) had been added. The mixture was heated on a water-bath for 30 min and poured into ice-water (100 ml). A white, fluffy precipitate was formed, which, when recrystallised twice from ethanol formed light yellow needles, m.p. 141°C. (Found: C 39.1; H 2.9; Br 29.1. Calc. for $C_{18}H_{16}O_{10}Br_2$: C 39.1; H 2.9; Br 29.0.) The substance gave a precipitate with 2,4-dinitrophenylhydrazine, but did not dissolve in cold aqueous sodium hydroxide.

Ozonide of tetrabromo derivative. IV (0.7 g) was dissolved in ethyl acetate (100 ml) and ozonised as described above. The yellowish crude ozonide was washed with ethanol and became then white. It was dissolved in acetone, filtered and the solution was concentrated slowly. Colourless crystals separated. M.p. 131°C. (Found: Act. O 4.3. Calc. for $C_{18}H_{14}O_{12}Br_4$: Act. O 4.3.) The ozonide was reduced and worked up as described above. Yellow needles, m.p. and mixed m.p. with V 132°C. The ethanol used for washing the crude ozonide was concentrated and yellow crystals (0.6 g) were formed. These were washed with water, dissolved in acetone and filtered. A slow evaporation afforded a yellow substance m.p. ca. 70°C. (Found: Act. O 2.3. Calc. for $C_{18}H_{14}O_6Br_4$: Act. O 2.3.)

Ozonide of dichloro derivative. II (3.0 g) was dissolved in ethyl acetate (150 ml) and ozonised as described above. The ozonide (2.7 g) was recrystallised from aqueous acetone. M.p. 143°C. (Found: C 43.6; H 3.4; Cl 14.8; act. O 6.4; M (acetone) 507. Calc. for $C_{18}H_{16}O_{12}Cl_2$: C 43.7; H 3.3; Cl 14.3; act. O 6.5, M 495.)

The ozonide (3.0 g) was reduced with sodium iodide and worked up as already described. Yield 0.4 g of yellow needles. M.p. 120°C. (Found: C 43.8; H 3.3; Cl 18.6. Calc. for $C_{14}H_{12}O_8Cl_2$: C 44.3; H 3.2; Cl 18.7.) The substance gave a precipitate with 2,4-dinitrophenylhydrazine and a yellowish-brown colour with ferric chloride.

1. Ikuta, M. *J. prakt. Chem.* [2] **45** (1892) 65.
2. Bernatek, E. and Thoresen, F. *Acta Chem. Scand.* **9** (1955) 743.
3. Bernatek, E. and Thoresen, F. *Acta Chem. Scand.* **13** (1959) 342.

Received January 24, 1961.