SYNTHESES OF METHYL-2-FURYLKETONES

XIII. ω,ω-Dihalogenomethyl-2-Furylketones and their 5-Nitro Derivatives. 5-Nitro-2-Furylglyoxal*

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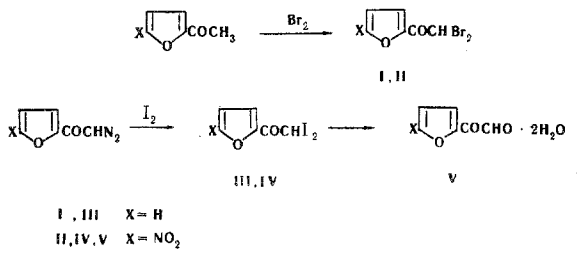
ω, ω-Dibromomethyl-2-furylketone and its 5-nitro derivatives are prepared by brominating the appropriate ketones in CCl_4. ω, ω-diiodomethyl-2-furylketone and its 5-nitro derivative are synthesized by the action of iodine on the appropriate diazoketones, and in the case of the 5-nitro derivative along with the diiodoketone is isolated the corresponding glyoxal. 5-Nitro-2-furylglyoxal is also obtained by the action of dimethylsulfoxide on bromomethyl-5-nitro-2-furylketone.

Continuing research on the synthesis and transformations of furan halogenoketones [1–5], dihalogenomethyl-2-furylketones and their 5-nitro derivatives are now synthesized.

ω, ω-Dibromomethyl-2-furylketone I and its 5-nitro derivative II are obtained by brominating the corresponding ketones with bromine, in carbon tetrachloride. Under those conditions I is obtained in the same yield as when brominating in carbon disulfide [6]. ω, ω-Diiodomethyl-2-furylketone III and its 5-nitro derivative IV are synthesized by



the action of iodine on the diazoketones. Reaction with diazomethyl-5-nitro-2-furylketone was considerably slower than with diazomethyl-2-furylketone, e. g. in ether at 25° C it was incomplete even after a week, so the reaction was run in boiling carbon tetrachloride. A similar retardation of reaction is also observed when introducing the nitro group into ω-diazoacetophenone [7].

The resultant dihalogenoketones have low stabilities. Dibromo- and diiodomethyl-2-furylketone, like bromomethyl-2-furylketone [3, 4], are converted to black solid polymers on keeping. Introduction of a nitro group into the furan ring favors polymerization, and furthermore favors conversion to glyoxal derivatives. For example the action of iodine on diazomethyl-5-nitro-2-furylketone gives, along with the diiodoketone, 5-nitro-2-furylglyoxal (VI), which we previously obtained [8] by oxidizing methyl-5-nitro-2-furylketone, as well as through the appropriate ketoaldonitrone. With free access of air to the apparatus, only the glyoxal V was formed. We have also prepared it, analogously to [9], by treating bromomethyl-5-nitro-2-furylketone with dimethylsulfoxide.

EXPERIMENTAL

Dibromomethyl-2-furylketone (I). 32 g (0.2 mole) Bromine was added, in 30 min, to a solution of 11.0 g methyl-2-furylketone in 50 ml dry CCl_4 at room temperature, the mixture left until evolution of HBr ceased, poured into ice-water, the oil separated off, and vacuum-distilled, to give 22.8 g (88%) of I, bp 135° C (12 mm) [145°–147° C (15 mm) [6]]. Found: C 27.14; H 1.80; Br 59.61%. Calculated for $C_6H_4Br_2O_2$: C 26.89; H 1.50; Br 59.58%.

Dibromomethyl-5-nitro-2-furylketone (II). 15.5 g (0.1 mole) Methyl-5-nitro-2-furylketone was brominated with 32 g (0.2 mole) bromine in 50 ml dry CCl_4 at 50° C. II was isolated by the procedure described above. Yield 20.5 g (73.5%), mp 141°–143° C (7–8 mm). Found: C 22.63; H 1.14; Br 51.29; N 4.51%. Calculated for $C_6H_3Br_2NO_4$: C 23.03; H 0.97; Br 51.08; N 4.78%.

Diiodomethyl-2-furylketone (III). A solution of 20.32 g (0.08 mole) iodine in 100 ml dry ether was added to a solution of diazomethyl-2-furylketone [10] at room temperature. When vigorous evolution of N ceased, e. g. after about an hour, the contents of the flask were refluxed for 1 hr, then washed with conc. Na thiosulfate solution, and next with water. Yield 13.7 g (47%), long pale-yellow plates, mp 85°–86° C (ex EtOH). Found: C 20.07; H 1.13; I 68.83%. Calculated for $C_6H_4I_2O_2$: C 19.69; H 1.09; I 69.38%. Readily soluble in hot EtOH, somewhat less soluble in cold EtOH, insoluble in water, on prolonged keeping it was transformed to a black glistening solid.

Reaction of diazomethyl-5-nitro-2-furylketone with iodine. 1.81 g (0.01 mole) Diazomethyl-5-nitro-2-furylketone [3]. 2.54 g (0.01 mole) iodine, 100 ml ether, and 70 ml dry CCl_4 were refluxed together for 4 hr 30 min. After cooling the precipitate was filtered off and washed with ether, yield 0.80 g 5-nitro-2-furylglyoxal dihydrate V, mp 95°–96° C (ex water). Found: C 35.47; H 3.47; N 6.80%. Calculated for $C_6H_3NO_5 \cdot 2H_2O$: C 35.11; H 3.43; N 6.82%. After evaporating off the solvent, the filtrate gave 3.0 g brown syrupy product, permeated by nodules of colorless plate-shaped crystals. After purifying by dissolving in glacial AcOH and precipitating with water, it

*For Part XII see [1]

formed pale-yellow needles, diiodomethyl-5-nitro-2-furylketone (IV), mp 72°–73° C. Found: C 17.62; H 0.91; N 3.22; I 61.47%. Calculated for $C_6H_3I_2NO_4$: C 17.71; H 0.74; N 3.44; I 62.35%.

5-nitro-2-furylglyoxal dihydrate (V). a) Prepared, without IV as impurity, from diazomethyl-5-nitro-2-furylketone and iodine, as described above, but using boiling for 2 hr, and leaving for 2 weeks with access of air. 70% yield, mp 95°–96° C (ex water).

b) 11.4 g (0.05 mole) Bromomethyl-5-nitro-2-furylketone was dissolved in 60 ml dimethylsulfoxide, allowed to stand for 20 hr, then diluted with 350 ml water, and the mixture extracted with 350 ml ether. After distilling off the ether, 6.0 g (59%) product was obtained, mp 95° C (ex water), identical with the preparation obtained by oxidizing methyl-5-nitro-2-furylketone [8].

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