BRIEF COMMUNICATIONS

SYNTHESES OF METHYL-2-FURYLKETONES

XII. ω-Derivatives of Methyl-5-Bromo-2-Furylketone*

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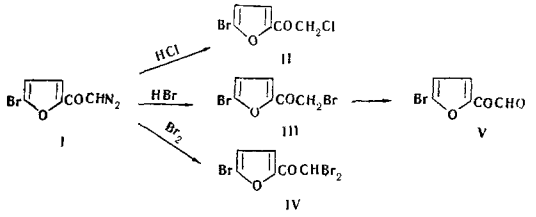
ω-Chloro, ω-bromo, and ω,ω-dibromo derivatives of methyl-5-bromo-2-furylketone are synthesized from diazomethyl-5-bromo-2-furylketone. 5-Bromo-2-furylglyoxal is prepared by the action of dimethylsulfoxide on the ω-bromo derivative. It is converted to 3-(5'-bromofuryl-2')quinoxal-2-one.

Continuing previously published work on the synthesis of halogeno-methylketones of the furan series [2–4] based on diazomethyl-5-bromo-2-furylketone I, ω-chloro II, ω-bromo III and ω, ω-dibromo derivatives IV of methyl-2-furylketone have been prepared.



I is prepared from 5-bromo-2-furoylchloride and diazomethane, III is identical with the preparation obtained by brominating methyl-5-bromo-2-furylketone with bromine in carbon disulfide [5]. By analogy with [6], the action of dimethylsulfoxide on III gives 5-bromo-2-furylglyoxal. Reaction of the latter with o-phenylenediamine gives 3'-(5'-bromofuryl-2')quinoxal-2-one VI.

EXPERIMENTAL

Diazomethyl-5-bromo-2-furylketone (I). 20.9 g (0.1 mole) 5-Bromo-2-furoylchloride [7] in 150 ml ether was added to 450 ml of an ether solution of diazomethane, prepared from 35 g (0.34 mole) nitrosomethylurea, at 5° C, the mixture left overnight in the cold, and the ether then distilled off. Yield 18.9 g (88%), mp 91°–92° C (ex EtOH). Found: C 33.56; H 1.35; Br 37.02%. Calculated for $C_6H_3BrN_2O_2$: C33.51; H 1.45; Br 37.17%.

Bromomethyl-5-bromo-2-furylketone (III). 4.3 g (0.02 mole) I was dissolved in 50 ml ether, 3.7 ml HBr added carefully at room temperature, the mixture left overnight, excess ether distilled off, the solid filtered off with suction. Yield 4.3 g (80%), mp 98°–99° C (ex benzene + petrol ether, or ex EtOH) (mp 98.5°–99.5° C [5]). Found: C 27.03; H 1.69; Br 59.20%. Calculated for $C_6H_4Br_2O_2$: C 26.89; H 1.50; Br 59.58%.

Chloromethyl-5-bromo-2-furylketone (II). 21.5 g (0.1 mole) I was dissolved in 200 ml ether, and the solution saturated with dry HCl. The mixture was worked up as described under III, yield 11.6 g (52%), mp 91°–93° C (ex EtOH). Found: C 32.45; H 1.93; Br+Cl 51.33%. Calculated for $C_6H_4BrClO_2$: C 32.25; H 1.80; Br+Cl 51.63%.

Dibromomethyl-5-bromo-2-furylketone (IV). 6.5 g (30 mM) I was dissolved in 100 ml dry CCl_4, heated to 50° C, 10.6 g (66 mM) bromine added, and the whole left overnight at room temperature. After distilling off the solvent, a cut bp 125°–130° C (3 mm) was taken, yield 4.3 g (58%). Found: C 21.50; H 1.06; Br 68.93%. Calculated for $C_6H_3Br_3O_2$: C 20.78; H 0.87; Br 69.15%.

5-Bromo-2-furylglyoxal (V). 1.1 g (4 mM) III was dissolved in 3 ml dimethylsulfoxide and left overnight at room temperature, diluted with 15 ml water, and extracted with ether. Evaporation of the ether gave 0.5 g (60%) V, mp 81°–83° C (ex dilute EtOH). Found: C 35.59; H 1.89; Br 39.80%. Calculated for $C_6H_3BrO_3$: C 35.49; H 1.49; Br 39.37%.

3-(5'-Bromofuryl-2')quinoxal-2-one (VI). Prepared by boiling V with o-phenylenediamine in EtOH, colorless crystals, mp 124° C (ex EtOH). Found: C 49.70; H 2.69; N 9.90%. Calculated for $C_{12}H_7BrN_2O_2$: C 49.51; H 2.42; N 9.62%.

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*For Part XI see [1].

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