LETTERS TO THE EDITOR

5-SODIO-2-DIETHOXYMETHYLFURAN

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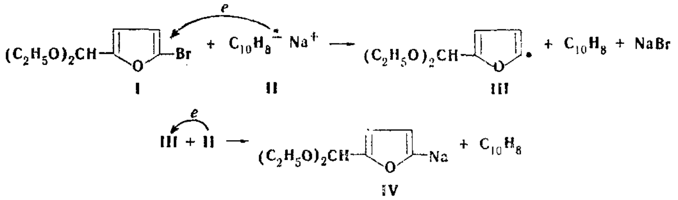
Organosodium compounds of the furan series that contain active functional groups have not been described. We have established that 5-sodio-2-diethoxymethylfuran (IV) is formed as a result of the reaction of 5-bromo-2-diethoxymethylfuran (I) with naphthylsodium (II) in tetrahydrofuran at −20°C. Compound IV is converted to the known 5-formylpyromucic acid by carbonation and subsequent hydrolysis in slightly acidic media. Since naphthylsodium can give up only one electron, which is situated in the lower antibonding π orbital of the molecule, the reaction apparently proceeds through a step involving the following two one-electron transfers:



Compound IV is also formed by the action of phenylsodium on I, but this reaction is complicated by side processes to a greater degree than the previous one.

EXPERIMENTAL

5-Bromo-2-diethoxymethylfuran (I). A mixture of 9 g (51 mmole) of 5-bromofurfural [1], 11 g (74 mmole) of ethyl orthoformate, 15 ml of absolute alcohol, and 0.5 ml of a saturated alcohol solution of hydrogen chloride was refluxed for 1.5 h. The alcohol was removed by distillation, and the residual I was vacuum-distilled to give 10 g (78%) of a product with bp 128-130° (18 mm). Found: C 43.1; H 5.6; Br 32.4%. $C_9H_{13}BrO_3$. Calculated: C 43.4; H 5.3; Br 32.1%.

5-Sodio-2-diethoxymethylfuran (IV). A) A mixture of 0.36 g (0.016 g-atom) of powdered sodium and 2.1 g (16 mmole) of sublimed naphthalene in 30 ml of tetrahydrofuran was stirred under nitrogen at 30-35° for 2 h. The green solution of naphthylsodium was then cooled to −20°, and 1.8 g (7 mmole) of I in 5 ml of tetrahydrofuran was added to it. When all of the I had been added, the coloration due to naphthylsodium vanished. To determine the yield of IV, it was carbonated with dry ice, after which the tetrahydrofuran was removed by distillation. Ether (20 ml) and 30 ml of water were added to the residue, and the aqueous layer was separated and acidified with 10% hydrochloric acid. After 10 min, the 5-formylpyromucic acid was extracted several times with ether. The ether was removed by distillation to give 0.43 g (42%) of 5-formylpyromucic acid with mp 202-203° (from water) (mp 204° [2]). The oxime melted at 224-225°, in agreement with the melting point indicated in [3].

B) A solution of 2.5 g (10 mmole) of I in 10 ml of toluene was added at −20° to phenylsodium obtained from 0.6 g (0.025 g-atom) of sodium and 1.4 g (12 mmole) of chlorobenzene in 20 ml of toluene [4]. The mixture was stirred for 30 min and carbonated with dry ice. The yield of 5-formylpyromucic acid was 0.21 g (15%).

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