Synthesis of 4-Imidazolin-2-ones *via* the Birch Reduction of Hydantoins

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The reduction of 5-(5-methyl-2-furyl)hydantoin to 4-(5-methyl-2-furyl)-4-imidazolin-2-one is described.

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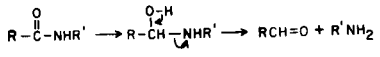
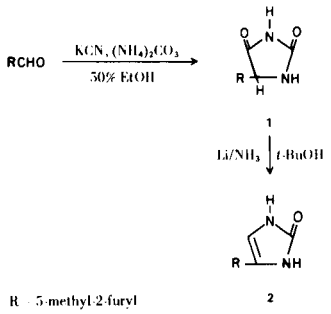
The Birch reduction of amides to aldehydes (or alcohols) and amines is known (1,2).



There has been no report, however, on the behavior of hydantoins, *i.e.* urea derivatives, in dissolving metal reductions. We now wish to report the selective reduction of an amide linkage in an hydantoin ring.

The reaction of 5-(5-methyl-2-furyl)hydantoin (**1**) with five equivalents of lithium in *t*-butyl alcohol and liquid ammonia resulted in the isolation of 4-(5-methyl-2-furyl)-4-imidazolin-2-one (**2**). As hydantoins are easily synthesized from the corresponding aldehydes (3,4), this sequence provides a convenient high yield route to 4-substituted 4-imidazolin-2-ones from simple, readily available precursors.



The urea carbonyl should exist predominantly in the enolic anion form (**3a** or **3b**) and would therefore be protected against reduction. When methanol was used in-

stead of *t*-butyl alcohol, a mixture of reduced products was obtained. This result was attributed to the greater acidity of methanol which consequently effects protonation of all anions and causes ring cleavage as well as reduction.

EXPERIMENTAL

Melting points were determined in open capillaries on a Thomas-Hoover melting point apparatus and are corrected. Infrared spectra were recorded with a Perkin-Elmer 137 spectrophotometer. Pmr spectra were determined on a Varian A-60A spectrometer with TMS as an internal standard. Mass spectra were obtained on a Finnigan Model F-3300 mass spectrometer with data system 6000. Elemental analyses were carried out by Robertson Laboratory, Florham Park, New Jersey.

5-(5-Methyl-2-furyl)hydantoin (**1**).

5-Methyl-2-furfural (4.5 g., 0.04 mole) was shaken with 20 ml. saturated sodium bisulfite to give white crystals of α-hydroxy-5-methyl-2-furanmethanesulfonate (8.5 g., 0.04 mole) which were filtered and washed with 5 ml. of ethanol and 5 ml. of ether to remove contaminants. The bisulfite addition product was added to a suspension of potassium cyanide (5.20 g., 0.08 mole) and ammonium carbonate (15.36 g., 0.16 mole) in 100 ml. of 50% aqueous ethanol. The reaction mixture was heated 4 hours at 55-60° and one hour at 70-80°, whereupon it was acidified with 20 ml. 6 *N* hydrochloric acid and maintained at 70-80° for one hour longer. Filtration of the reaction mixture afforded 5-(5-methyl-2-furyl)hydantoin (5 g., 0.027 mole, 70% yield), m.p. 135-139°; nmr (DMSO-d_6): δ 2.25 (s, 3H), 5.21 (2, 1H), 6.0-6.15 (m, 1H), 6.38 (d, 1H), 8.23 (s, broad, 1H), and 10.78 (s, broad, 1H); ir (potassium bromide): 3300 and 1721 cm^{-1}; uv (ethanol): λ max 222 nm.

Anal. Calcd. for $C_8H_8N_2O_3$: C, 53.33; H, 4.44; N, 15.55. Found: C, 53.19; H, 4.56; N, 15.34.

4-(5-methyl-2-furyl)-4-imidazolin-2-one (**2**).

5-(5-Methyl-2-furyl)hydantoin (**1**) (2.23 g., 0.0124 mole) was dissolved in a solution of 15 ml. of *t*-butyl alcohol and 100 ml. of dry liquid ammonia at -33°. Lithium (0.4 g., 0.062 gram atoms) was added to this solution over a period of 0.5 hour. Upon completion of the addition, the ammonia was allowed to evaporate overnight. The residue was dissolved in 50 ml. of water and acidified to *p*H 3. Recrystallization of the resulting yellow solid either from 50% ethanol or acetonitrile afforded 4-(5-methyl-2-furyl)4-imidazolin-2-one (**2**) (1.62 g., 0.00992 mole, 80% yield) as yellow crystals, m.p. 237.5-239°; nmr (DMSO-d_6): δ 2.26 (s, 3H), 6.08 (d, 1H), 6.39 (d, 1H), 6.52 (s, 1H), 10.10 (s, broad, 1H), and 10.50 (s, broad, 1H); ir (potassium bromide) 3090, and 1695 cm^{-1}; uv (ethanol): λ max 283 nm. High resolution mass spectrum M+, m/e 164.0584, calculated molecular weight 164.0585 ($C_8H_8N_2O_2$).

Anal. Calcd. for $C_8H_8N_2O_2$: C, 58.53; H, 4.91; N, 17.06. Found: C, 58.59; H, 5.09; N, 16.93.

REFERENCES AND NOTES

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