Tetrahedron Letters, Vol. 34, No. 33, pp. 5221-5222, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

Synthesis and Ene Reactions of 3-Methylene-2,3-Dihydrofuran

William H. Miles,* Christina L. Berreth and Patricia M. Smiley

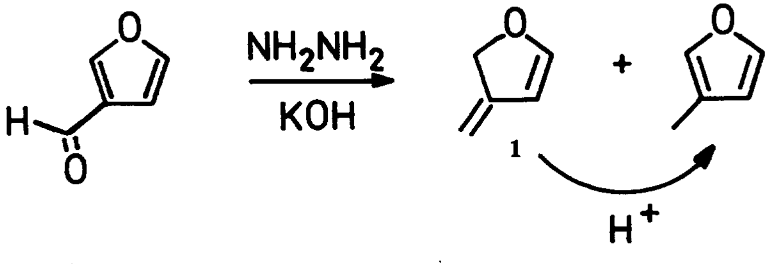
Department of Chemistry, Lafayette College, Easton, PA 18042

Key Words: Wolff-Kishner reduction, ene reaction, 3-alkylidene-2,3-dihydrofuran, 3-substituted furan.

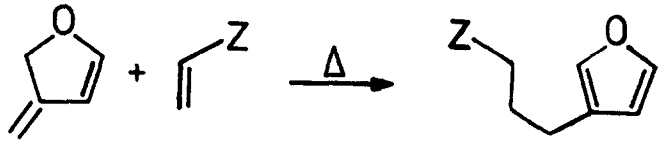
Abstract: *The unexpected formation of 3-methylene-2,3-dihydrofuran 1 using the Huang-Minlon modification of the Wolff-Kishner reduction of 3-furaldehyde is described. Furan 1 readily undergoes ene reactions with simple electron-deficient alkenes.*

Alicyclic isomers of aromatic compounds are fascinating molecules which have been the subject of numerous synthetic and theoretical investigations.[1] Although most studies have been concerned with the isomers of toluene and benzoannelated toluenes, there are scattered reports describing the synthesis and chemistry of the alicyclic isomers of furan compounds.[2] This communication describes the serendipitous synthesis of the simplest member of the 3-alkylidene-2,3-dihydrofuran family, 3-methylene-2,3-dihydrofuran 1.

The Wolff-Kishner reduction (Huang-Minlon modification)[3] of 3-furaldehyde gave 1 and 3-methylfuran in variable proportions. The optimum conditions give a 4:1 mixture of 1:3-methylfuran in 75% yield which was readily characterized by IR and NMR.[4] Purification of 1 has not been possible without substantial loss of material due to isomerization to 3-methylfuran and polymerization. Furan 1 is extremely acid-sensitive; a trace of trifluoroacetic acid gives 3-methylfuran in quantitative yield.



Although the acid sensitivity of furan 1 precludes reaction conditions which employ or generate acid, we anticipate that 1 will be a potentially useful starting material for the synthesis of furans. For example, the ene reaction[5] of 1 (as a 4:1 mixture with 3-methylfuran) with mono-substituted enophiles (Z = $COCH_3$, CN, $CO_2CH_2CH_3$, 3 equivs.; CH_2Cl_2; 24-96 hrs; 40°C) gave 3-substituted furans 2 (50-80% yield).[6] As in the case for the related 5-methylene-1,3-cyclohexadiene (*o*-isotoluene), the driving force for the relatively rapid ene reactions of 1 appears to be the formation of the aromatic system.[1b]



1

2

The reported procedure offers a convenient and practical synthesis of the simplest member of the 3-alkylidene-2,3-dihydrofuran family. Further synthetic applications of **1** to the synthesis of substituted furans will be reported in due course.

Acknowledgements: We gratefully acknowledge the generous financial support of Lafayette's Committee on Advanced Study and Research in the form of a summer and academic year stipend to CLB.

References and Notes:

1. (a) Bailey, W. J.; Baylouny, R. A. *J. Org. Chem.* **1962**, *27*, 3476. (b) Gajewski, J. J.; Gortva, A. M. *J. Org. Chem.* **1989**, *54*, 373. (c) Bartmess, J. E.; Griffith, S. S. *J. Am. Chem. Soc.* **1990**, *112*, 2931. (d) Andemichael, Y. W.; Wang, K. K. *J. Org. Chem.* **1992**, *57*, 796.
2. Tsuji, J.; Watanabe, H.; Minami, I.; Shimizu, I. *J. Am. Chem. Soc.* **1985**, *107*, 2196. Minami, I.; Yuhara, M.; Tsuji, J. *Tetrahedron Lett.* **1987**, *28*, 629. Trahanovsky, W. S.; Cassady, T. J.; Woods, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 6691. Kaydos, J. A.; Spencer, T. A. *J. Org. Chem.* **1991**, *56*, 425. Reich, H. J.; Yelm, K. E.; Wollowitz, S. *J. Am. Chem. Soc.* **1983**, *105*, 2503. Usami, T.; Shirai, N.; Sato, Y. *J. Org. Chem.* **1992**, *57*, 5419.
3. Todd, D. *Org. React.* **1948**, *4*, 378.
4. In a 100 mL 3-neck round-bottom flask equipped with a short-path distillation head, a thermometer and a stopper was charged ethylene glycol (75 mL, 0.5% H_2O), 3-furaldehyde (3.15 mL, 37 mmol) and hydrazine (1.25 mL, 40 mmol). After stirring for 15 min, KOH (5.5 g, 98 mmol) was added and the reaction mixture was heated to 140-155°C. Vigorous gas evolution commenced at 130°C, and a distillate containing water and the furans was collected. The bottom aqueous layer was removed by Pasteur pipette, and the furans were dried over $MgSO_4$. Typical crude yields of the furans were 70-80%. For **1**: ^{1}H NMR (300 MHz, $CDCl_3$) δ6.76 (1H, br s), 5.59 (1H, d, J=2.2 Hz), 4.89 (2H, t, J=2.9 Hz), 4.71 (1H, t, J=2.9 Hz), 4.56 (1H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ155.0, 149.2, 106.7, 95.0, 73.6; IR (neat) 3089, 2931, 2868, 1628, 1578, 1450 cm^{-1}.
5. Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556. Mikami, K.; Shimizu, M. *Chem. Rev.* **1992**, *92*, 1021.
6. Furans **2** were fully characterized. For example, spectral data for 5-(3-furyl)-2-pentanone: ^{1}H NMR ($CDCl_3$, 300 MHz) δ7.35 (1H, s), 7.21 (1H, s), 6.26 (1H, s), 2.4 (4H, m), 2.12 (3H, s), 1.84 (2H, pentet, J=7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ201.2, 142.7, 138.9, 124.1, 110.7, 42.7, 29.8, 23.9, 23.7; IR (CH_2Cl_2) 1713 cm^{-1}.

(Received in USA 1 June 1993; accepted 18 June 1993)