Tetrahedron Letters No. 42, pp 3619 - 3620, 1975. Pergamon Press. Printed in Great Britain.

THE FORMATION OF METHYLENE DIHYDROFURANS BY THE *T*-BUTYLATION OF ALKYL FURANS: STABLE METHYLFURANS TAUTOMERS

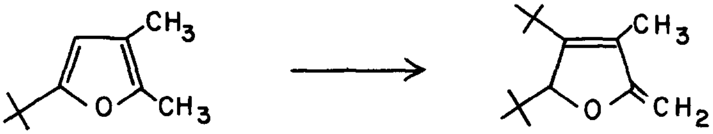
Hans Wynberg and U.E. Wiersum[1,2]

Department of Organic Chemistry, The University, Groningen, The Netherlands

Received in UK 2nd September 1975; accepted for publication 4th September 1975)

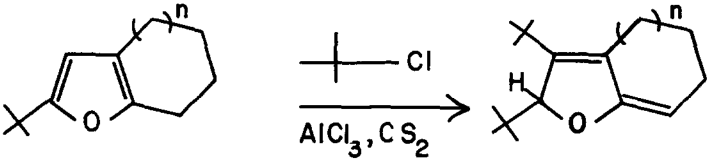
When 2,5-di-*t*-butylfuran is treated with *t*-butylchloride under Friedel-Crafts conditions, 2,3,5-tri-*t*-butylfuran is formed in 85% yield[3]. We have made a brief study of this rather unique reaction and have discovered that, when the appropriate structural features are present, ortho-*t*-butylation takes place in such a manner as to minimize the steric interference, even at the expense of the aromaticity of the furan ring.

Thus, when 5-*t*-butyl-2,3-dimethylfuran (I) was treated with *t*-butyl chloride and a molar equivalent of aluminum chloride in carbon disulfide at 0°C, 2,3-di-*t*-butyl-4-methyl-5-methylene-2,5-dihydrofuran (II) was isolated as a colorless liquid in 76% yield[4].



I II

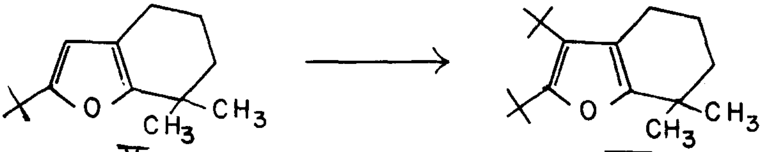
The reaction appears to be general, applying also to cycloalkyl(b)furans III:



III a, n=1
b, n=2

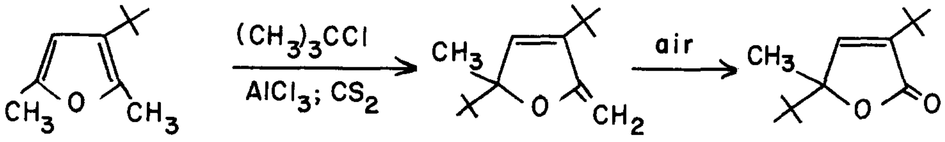
IV a, n=1 35%
b, n=2 60%

Normal ortho-*t*-butylation occurs when the exomethylene structure cannot be formed[5]:



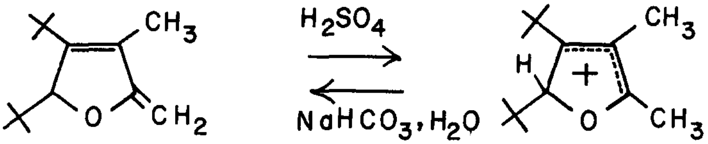
V VI

Attempts to prepare the unknown 3,4-di-*t*-butylfurans failed. Instead, the dihydrofuran VIII was isolated in 71% yield. The latter compound readily oxidizes to the butenolide[6] IX.



VII VIII IX

All of the exomethylene-2,5-dihydrofurans are *reversibly* protonated in 96% sulfuric acid forming the stable yellow furanonium ions, e.g. X, attesting to the key role of the *t*-butyl group[6].



II X

Acknowledgements. H. Wynberg gratefully acknowledges a Hill Foundation Visiting Professorship at the University of Minnesota during spring quarter, 1975, which enabled him to complete this communication, and the able assistance of P.L. Espeland.

References and Footnotes.

1. In part from the doctoral dissertation of U.E. Wiersum, Groningen, Holland, 1968.
2. Present address, AKZO, NV. Arnhem, Holland.
3. H. Wynberg and U.E. Wiersum, *Chem. Comm.*, 1, 1 (1965).
4. All new compounds gave C and H values within 0.3% of those calculated. The *t*-butylfurans were prepared by alkylation of the appropriate enamine with bromopinacolone followed by ringclosure with P_2O_5. Yields were good. U.V. maxima of the exomethylene compounds (II, IVa, IVb, VIII) ranged from 262-270nm (log E 3.9-4.1); NMR (τ, TMS = 10); 8.76-9.13 (*t*-butyl); 4.64-5.80 (methylene); 4.14-4.99 (ring proton).
5. NMR (τ, TMS = 10) H(2) 3.06-3.52 (no rapid exchange with D_2SO_4); H(4) 0.4-2.34; H(*t*-butyl) 7.93-8.33.
6. K.B. Wiberg and T.W. Hutton, in *J. Amer. Chem. Soc.*, 76, 5376 (1954), describe the synthesis of a 2,4-di-*t*-butyl-$\Delta^{\alpha\beta}$-butenolide.
7. 2-methylene-2,5-dihydrofuran is converted to 2-methylfuran upon treatment with a trace of acid: H.L. Price, *J. Amer. Chem. Soc.*, 74, 3193 (1952).