HETEROCYCLES, Vol 15, No 2, 1981

THE BF_3-CATALYSED REACTION BETWEEN 2-METHYLFURAN AND SOME α,β-UNSATURATED CARBONYL COMPOUNDS.[1]

J. ApSimon*, V. Seenu Srinivasan, M.R. L'Abbé and R. Seguin

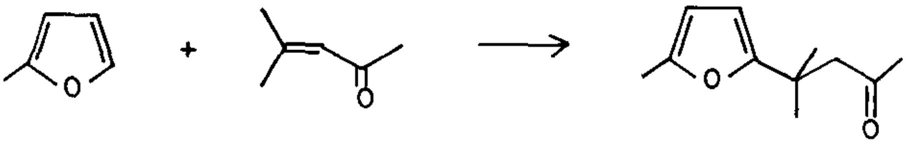
Department of Chemistry, Carleton University, Ottawa, Canada K1S 5B6

Abstract

The reaction of 2-methylfuran with some αβ unsaturated compounds in the presence of BF_3-etherate is described as well as studies of the cleavage of the furan ring of the products. Only 1,4-addition to the conjugated carbonyl system is observed even in the case of hindered species.

During the course of some synthetic studies aimed at the controlled cyclization of 1,4-polyketones we have reexamined the reaction of 2-methylfuran with a variety of αβ-unsaturated ketones or aldehydes. At the same time we were interested in the possibility of Lewis acid catalysed Diels-Alder reactions of furans with such olefins (1).

In no case could we detect any cycloaddition reaction, but rather the Michael-type addition at the least hindered α position of the furan was noted when BF_3 was used as a catalyst. Thus, 2-methylfuran reacts with mesityl oxide in methylene chloride containing BF_3-etherate to yield, after isolation, up to 71% of adduct 1.[2] Adducts 2 and 3 were obtained in similar yields from reaction with crotonaldehyde and methyl vinyl ketone respectively. No reaction was observed in the absence of Lewis acid.

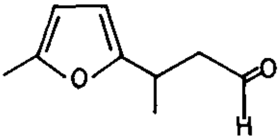


1

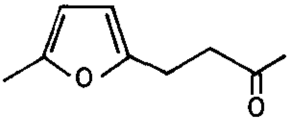
---

[1] Dedicated to Prof. T. Kametani on the occasion of his retirement from the chair of Organic Chemistry at the Pharmaceutical Institute of Tohoku University.

[2] All compounds described herein afforded proper combustion or exact mass spectral analysis as well as the expected IR and NMR spectra.



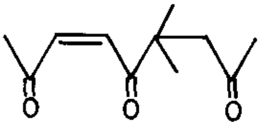
2



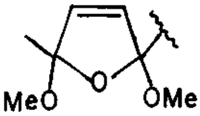
3

Similar products have been reported in a number of cases (2) from reaction of 2 methylfuran with a variety of αβ-unsaturated carbonyl compounds using mineral acids as catalysts although the yields reported appear to be inferior to our own observations.

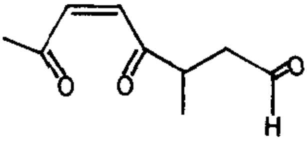
A variety of techniques were examined for the conversion of compounds 1-3 into triketones and their further conversions into species suitable for natural product synthesis (3,4), (e.g. Collins reagent, chromic acid oxidation,mineral acid hydrolysis, lead tetraacetate, in situ ketal formation, 1,4-dimethoxylation.) Oxidative methoxylation with bromine in methanol (4) proved to be the only technique that provided any success and that was observed only with the mesityl oxide adduct 1 when about 15% of the highly unstable enetrione 4 was isolated after acetic acid hydrolysis of the addition product (presumably 5). No useful chemistry on this compound emerged from these studies. We were able to detect (< 2% yield, spectroscopic evidence), the enedioneal 6 from the oxidative methoxylation-cleavage of the crotonaldehyde adduct 2.



4

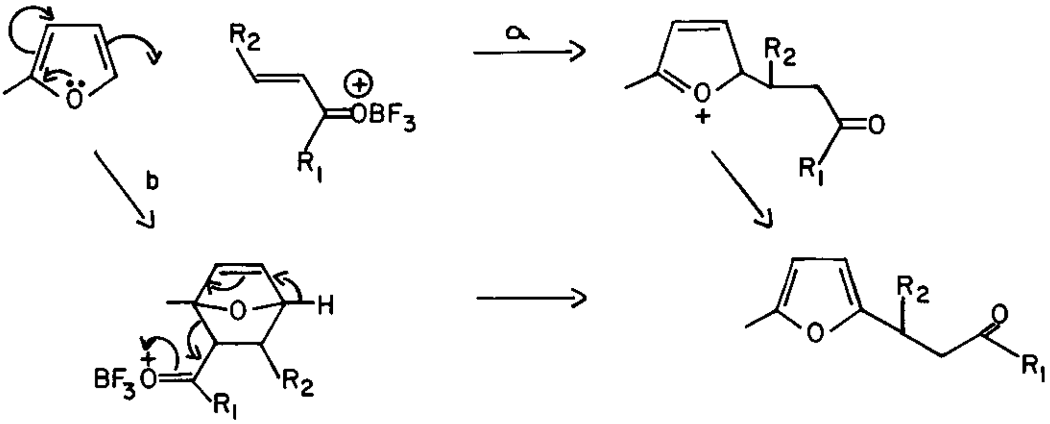


5



6

It is mechanistically interesting that in these brief studies and in those previously reported (2), the only adducts observed from αβ-unsaturated carbonyl species are those resulting from 1,4-addition, even in the case of highly hindered enones (e.g. mesityl oxide). It is tempting to speculate that, rather than a Michael process (pathway a in Scheme), the reaction proceeds via initial Diels-Alder attack followed by bond cleavage and rearomatisation of the furan ring as indicated in the Scheme (pathway b). We are actively pursuing this possibility.



SCHEME

Acknowledgements

We thank the National Research Council of Canada and the Natural Sciences and Engineering Research Council of Canada for generous financial assistance of our research work.

References

1. A.S. Onishchenko, Diene Synthesis, Israel Program for Scientific Translations, Jerusalem, 1964, p 556; A.E. McCulloch and A.G. McInnes, Can. J. Chem., 49, 3152 (1971); F. Kienzle, Helv. Chim. Acta 58 1180 (1975).
2. Yu. K. Yur'ev, N.S. Zefirov, A.A. Shteinman and V.I. Ryboedov, Zhur Obsheii Khim, 30, 3755 (1960); N.I. Shuikin, A.D. Petrov, V.G. Glukhortsev, I.F. Bel'sku and G.E. Skobtsova, Izv. Akad. Nauk. S.S.R. Ser. Khim, (Eng. trans) 9 1584 (1964); Yu. K. Yur'ev, N.S. Zefirov and A.A. Shteinman, Zhur Obsheii Khim, 33, 1150 (1963); K. Alder and C-H Schmidt, Ber. 76B 183 (1943); Lambiotte et Cie. French Patent #972,652 (Chem. Abs., 47, 1744h (1953); M.A. Tobias, J. Org. Chem. 35, 267 (1970).
3. Inter alia: A.J. Birch, K.S. Keosh and V.R. Mamdapur, Aust. J. Chem., 26 2671 (1973); T. Kametani, H. Nemoto and K. Fukumoto, Heterocycles 2 639 (1974); R. Partch, Tetrahedron Letters 3071 (1964); H.C. Brown, C.P. Garg and K.-T. Lim, J. Org.Chem. 36, 387 (1971).
4. J. Levisalles, Bull. Soc. Chim. France 997 (1957).

Received, 22nd September, 1980