

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

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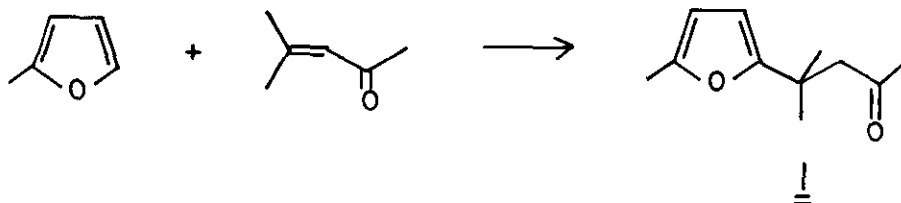
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Abstract

The reaction of 2-methylfuran with some $\alpha\beta$ 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.

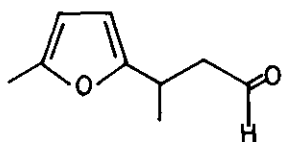
During the course of some synthetic studies aimed at the controlled cyclization of 1,4-polyketones we have reexamined the reaction of 2-methylfuran with a variety of $\alpha\beta$ -unsaturated ketones or aldehydes. At the same time we were interested in the possibility of Lewis acid catalysed Diels-Alder 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.

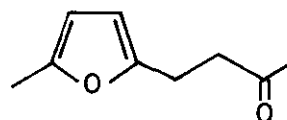


¹Dedicated to Prof. T. Kametani on the occasion of his retirement from the chair of Organic Chemistry at the Pharmaceutical Institute of Tohoku University.

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



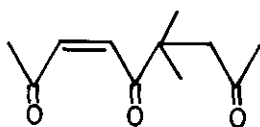
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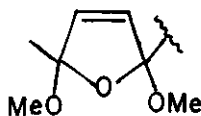
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Similar products have been reported in a number of cases (2) from reaction of 2-methylfuran with a variety of $\alpha\beta$ -unsaturated carbonyl compounds using mineral acids as catalysts although the yields reported appear to be inferior to our own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

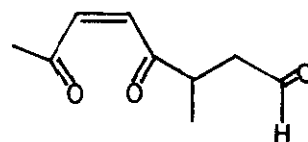
A variety of techniques were examined for the conversion of compounds 1-3 into triketones and their further conversions into species suitable for natural product synthesis (3,4), (e.g. Collins reagent, chromic acid oxidation, mineral acid hydrolysis, lead tetraacetate, *in situ* ketal formation, 1,4-dimethoxylation.) 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.



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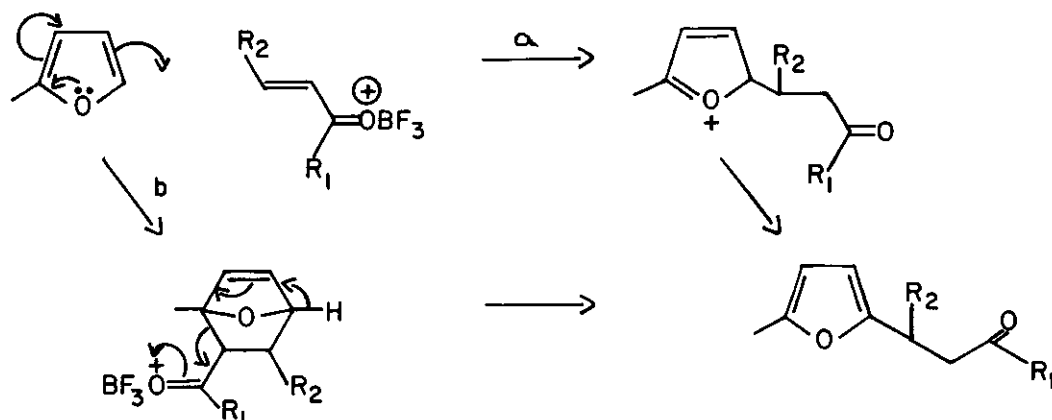


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It is mechanistically interesting that in these brief studies and in those previously reported (2), the only adducts observed from $\alpha\beta$ -unsaturated carbonyl species are those resulting from 1,4-addition, even in the case of highly hindered 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

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References

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