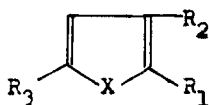


THE FREE RADICAL REACTIVITY OF METHYLATED FURANS AND THIOPHENES

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Recently we have studied the reactivity of methylated furans¹ and thiophenes² towards electrophilic as well as nucleophilic agents. Very little data on the free radical reactivity of these compounds exists and most of this deals with the radical bromination with *N*-bromosuccinimide in the presence of dibenzoyl peroxide³. Unfortunately these data disagree with the theoretical predictions of free radical reactivity. We have studied the free radical methylation of compounds I - IX with diacetyl peroxide. This method has been used several times for the study of free radical reactivity of substituted benzenes⁴⁻⁷ and its mechanism is well known⁸.



Compound	I	II	III	IV	V	VI	VII	VIII	IX
X	S	O	S	O	S	O	S	O	S
R ₁	H	Me	Me	H	H	Me	Me	H	H
R ₂	H	H	H	Me	Me	H	H	Me	Me
R ₃	H	H	H	H	H	Me	Me	Me	Me

The starting compounds were used as a solvent in each case. The data for all these reactions are summarized in Table 1.

Table 1.

Compound	Attack in position	Concentration of peroxide (mols)	Temperature °C	Time hrs.	Yield %
I	2	1	80	6	10
II	5	0.7	60	6	3.5
III	5	1	80	4	4
IV	2	0.7	60	6	10
	5				trace
V	2	1	80	4	9
	5				4.5
VI	3	0.7	80	4	trace
VII	3	1	80	4	trace
VIII	5	0.7	80	4	15
IX	5	1	80	4	21

The residue, after the most of unchanged starting compound had been distilled off through a 5-plate column, was analysed gas-chromatographically (Carbowax 20M, Neopentylglycolsebacate). All products were identified by the comparison of the GLC retention times and mass spectral data with those of authentic samples⁹. The products of radical attack at the methyl group were synthesised too, but not even a trace of these compounds could be detected in the reaction mixtures. Table 2 summarizes the theoretical and experimental data about the reactivity of the compounds studied. Our data are in very good agreement.

Table 2.

Compound	Relative Reactivity of Position ^a		
	Theoretical based on S_r^b	Experimental	
		NBS ^{3,10}	Methylation (this article)
I	2 > 3	2	2
II and III	5 > 3 > 4	2a > 5	5
IV and V	2 > 5 > 4	3a > 2 > 5	2 > 5
VI and VII	3=4 > 2a=5a	2a=5a	3=4
VIII and IX	5 > 2 > 2a > 4a		5

a) a denotes attack on a methyl group at the ring position indicated

b) The radical superdelocalisabilities (S_r) were calculated using the simple HMO method¹

The discrepancies with respect to the reaction of the studied compounds with NBS are due to the fact that this reaction does not proceed through the pure radical chain mechanism.³

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