Tetrahedron Letters No. 29, pp 2803 - 2804, 1973. Pergamon Press. Printed in Great Britain.

HYDROGEN-DEUTERIUM EXCHANGE IN SOME 2,4-DISUBSTITUTED THIOPHENES AND SELENOPHENES.

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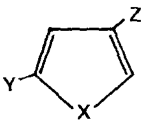
(Received in UK 12 April 1973; accepted for publication 14 June 1973)

We have recently shown that the reaction of CH_3O^- ions with various 2-Y-4-Z-disubstituted thiophenes and selenophenes 1 (X = S, Se ; Y, Z = NO_2, CN) results in the formation of stable Meisenheimer adducts (1). The magnitude of the coupling constant $J_{^{77}Se-H}$ allowed the structure 2 rather than the structure 3 to be attributed to the selenophenic complexes, and on grounds of analogy, the same would be expected for the thiophene complexes. However, we had no direct NMR evidence for the structure of the latter complexes.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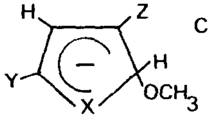
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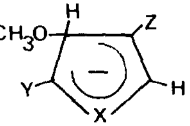
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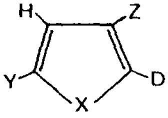
X = S, Se

Y, Z = NO_2, CN

In order to obtain such evidence, we prepared and investigated the corresponding 5- and 3-deuterated compounds. The results indicated a very rapid H/D exchange process at the 5-position which appears not to have been observed previously under such mild conditions in this type of heterocycles (2,3). Consequently, evidence for the structure of the thiophenic adducts cannot come from the study of 5-deuterated derivatives, contrary to claims in a recent communication concerning 2,4-dinitrothiophene (4). However, no exchange reaction occurs with the 3-deuterated compounds and their NMR spectra indicate the structure 2 for the adducts.

RESULTS.

The reaction of CH_3O^- ion with 5-deutero-2,4-Y,Z-thiophenes 4 in methanol or in methanol -DMSO-d_6 mixture does not give, as expected, a deuterated complex of structure 5 or 6, but an adduct having two ring protons and a methoxyl group. As shown by NMR, this adduct is identical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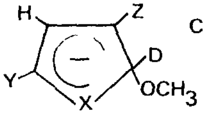
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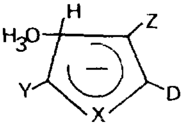
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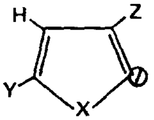
to that obtained from non-deuterated 2,4-Y,Z-thiophenes and must accordingly have the structure 2 or 3. Moreover, when the amount of added methoxide is less than one equivalent, the NMR spectrum shows also the formation of the non-deuterated parent heterocycle.

On the other hand, a monodeuterated complex is obtained when 1 is treated with one equivalent of CH_3O^- ion in CH_3OD or in a $CH_3OD/DMSO\text{-}d_6$ mixture.

These observations indicate the existence of a rapid exchange process between the H(5) ring proton and the hydroxyl group of methanol. The α position of thiophen is known to be more acidic than the β position (2,3) and, as noted with polynitrobenzenes (5,6), base-catalysed hydrogen-deuterium exchange involves probably the formation, at least in a small concentration, of a carbanionic intermediate 7.

Because of this exchange, it is clear that the structure of the Meisenheimer adducts cannot be deduced from the behavior of 5-deuterated derivatives. In contrast, it would be expected that 3-deuterated compounds would not exchange so readily and would be more suitable for a structure determination. This expectation was realized : when the reaction of CH_3O^- ion in CH_3OH with 8 was performed in $DMSO\text{-}d_6$, no exchange reaction was observed and the low-field portion of the NMR spectrum showed only a singlet at $\delta = 6.19$ppm, assignable to the proton attached to the sp^3 carbon of the monodeuterated adduct 9.



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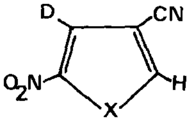

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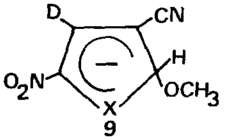

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From this result, the structure 2, where the sp^3 carbon is located in the position α to the sulfur atom can be unequivocally attributed to the thiophenic complexes.

It must be noted that the nucleophilic attack takes place at the 5-position, which is also the site of the proton abstraction leading to the presumed carbanion 7. Evidently, this position has more positive character and hence, both enhanced acidity as well as greater nucleophilic reactivity.

The reaction of CH_3O^- ions with 2,4-disubstituted selenophenes 1 (X = Se ; Y, Z = NO_2, CN) in CH_3OD also led to hydrogen / deuterium exchange at the α position and hence we can conclude that this exchange process offers a very easy and rapid route to some α-deuterated thiophenes and selenophenes. Further studies of the field are in progress.

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