

## NMR Study of the Behaviour of Some Methoxynitrothiophenes Toward Sodium Methoxide (1)

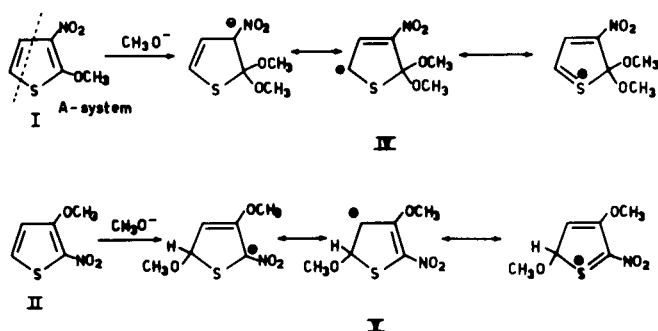
*Domenico Spinelli, Valeria Armanino and Antonino Corrao*

Institute of Organic Chemistry, University of Palermo

Sir:

In connection with previous work (2) on the nucleophilic reactivity of 5-membered ring systems, we have in progress research on the behaviour of various nitrothiophenes and selenophenes toward alkoxides, a problem which has received little attention (3).

This paper reports an NMR study (data summarized in the Table) of the reactions of 2-methoxy-3-nitrothiophene (I), 2-nitro-3-methoxythiophene (II) and 2-methoxy-5-nitrothiophene (III) with sodium methoxide. At room temperature I gives a Meisenheimer-type adduct at C<sub>2</sub> (IV) as supported by the appearance of a 6 proton singlet, whereas II furnishes an adduct at C<sub>5</sub> (V) as indicated by the appearance of two 3 proton singlets. Up to now we have no evidence for the formation of any adduct from III.



It must be noted that I and II represent the first methoxymononitro compounds containing no other activating group (withdrawing substituents, nitrogen atoms in heterocycle, etc.) for which there is evidence (4) for the formation of a Meisenheimer adduct. It is thought that this peculiar behaviour (5) may be attributed to the fact that the sulfur heteroatom plays an important role in its ability to accommodate a negative charge (6) and the site of attack (C<sub>2</sub> or C<sub>5</sub>) is related to the structure of the parent compounds.

The behaviour of I resembles that pointed out by Illuminati and coworkers (3b) in the case of 2-methoxy-3,5-dinitrothiophene; Meisenheimer complex formation from I at C<sub>2</sub> (the carbon having the methoxy group) must be related to the presence of the A-system. In fact II, in which this system is lacking, has a different behaviour as it undergoes direct nucleophilic attack on the free  $\alpha$ -position (C<sub>5</sub>), thus furnishing the first example of this type of reactivity in methoxymononitro compounds (7,8).

The observed coupling constants should be mentioned. The values measured for I-IV are somewhat higher than those reported in the literature (9) and this fact seems to be related to the nature of the substituents (10). A comparison between coupling constants of methoxynitrothiophenes and related complexes is very interesting. They are similar for the pair I and IV, whereas they are different for

TABLE (a)

Compound	Chemical Shifts ( $\tau$ , p.p.m.)			Coupling Constants (cps)	
	C <sub>3</sub> -H	C <sub>4</sub> -H	C <sub>5</sub> -H	C-OCH <sub>3</sub>	J <sub>34</sub> J <sub>45</sub>
I		2.71 (1H, d)	3.07 (1H, d)	5.85 (3H, s)	6.0
II		2.77 (1H, d)	1.99 (1H, d)	5.93 (3H, s)	6.1
III	3.44 (1H, d)	1.99 (1H, d)		5.95 (3H, s)	4.8
IV		3.67 (1H, d)	4.29 (1H, d)	6.75 (6H, s)	6.8
V		5.22 (1H, d)	4.40 (1H, d)	$\left\{ \begin{array}{l} 6.10 (3H, s) (b) \\ 6.37 (3H, s) (c) \end{array} \right.$	3.5

(a) Jeol C-60 instrument. Solutions (about  $1.5 \cdot 10^{-1}$  M) in DMSO, complex formation has been achieved by addition of one equivalent of sodium methoxide solution (about 5 M). On standing, solutions of complexes undergo exchange reactions and decomposition. In some instances the chemical shifts attributions have been made with the help of deuterated compounds. Numbers in parentheses represent relative intensities of the respective lines and their multiplicity. (b) C<sub>5</sub>-OCH<sub>3</sub>. (c) C<sub>3</sub>-OCH<sub>3</sub>.

II and V. The coupling constants value in V ( $J_{45} = 3.5$  cps) is very different from usual values of 2,3-disubstituted thiophenes ( $J_{45} = 5.4 \pm 0.6$  cps) (9). The difference in electronic distribution between II and V can perhaps affect the coupling constants (10), but it must be pointed out that the observed value resembles the value foreseen by means of Karplus' rule (11), for vicinal protons in cyclopentanes with a dihedral angle of about  $50^\circ$ . This datum, observed for the first time in a 5-membered heteroaromatic system (12), can be tentatively related to the fact that hybridization change at  $C_5$ , depending on attack of methoxide ion on this atom, makes the hydrogen atoms at  $C_4$  and  $C_5$  non-coplanar. This fact, which provides useful information about the tetrahedral structure of the complex at  $C_5$ , seems to be a valid confirmation of the assigned structure.

We thank the Italian Research Council (C.N.R.) for financial support.

#### REFERENCES

- (1) Presented at "Convegno di Chimica Organica, C.N.R." (Roma, 2-4 April 1970).
- (2) D. Spinelli, C. Dell'Erba and A. Salvemini, *Ann. Chim. (Rome)*, **52**, 1156 (1962); C. Dell'Erba and D. Spinelli, *Tetrahedron*, **21**, 1061 (1965); D. Spinelli, G. Guanti and C. Dell'Erba, *J. Heterocyclic Chem.*, **5**, 523 (1968); *Ric. Sci.*, **38**, 1048, 1051 (1968); C. Dell'Erba, D. Spinelli and G. Leandri, *Chem. Commun.*, 549 (1969); C. Dell'Erba, A. Guareschi and D. Spinelli, *J. Heterocyclic Chem.*, **4**, 438 (1967); D. Spinelli, G. Guanti and C. Dell'Erba, *Boll. Sci. Fac. Chim. Ind. Bologna*, **25**, 71 (1967).
- (3a) W. Steinkopf, *Ann. Chem.*, **513**, 285 (1934); S. Umezawa, *Bull. Chem. Soc. Jap.*, **12**, 4 (1937), *Chem. Abstr.*, **31**, 3913 (1937); (b) G. Doddi, G. Illuminati and F. Stegel, *Chem. Commun.*, 953 (1969).
- (4) E. Bunzel, A. R. Norris and K. E. Ressel, *Quart. Rev.*, **22**, 123 (1968); M. R. Crampton, *Adv. Phys. Org. Chem.*, **7**, 211 (1969); P. Buck, *Angew. Chem. Inter. Ed. Engl.*, **8**, 120 (1969).
- (5) It must be remembered that kinetic data (see reference 2) indicate that halogenonitrothiophenes are more reactive than isologous benzene compounds in nucleophilic substitutions. Nucleophilic reactivity and behaviour toward alkoxides seem to be two parallel aspects of the chemistry of thiophene compounds.
- (6) V. Schomaker and L. Pauling, *J. Am. Chem. Soc.*, **61**, 1769 (1939); H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **45**, 173 (1949); L. Melander, *Arkiv Kemi*, **8**, 361 (1955); D. T. Clark, *Tetrahedron*, **24**, 2567 (1968).
- (7) Compare with the similar behaviour with methoxide of *N,N*-dimethylpicramide [M. R. Crampton and V. Gold, *Proc. Chem. Soc.*, 298 (1964); *J. Chem. Soc. (B)*, 893 (1966); K. L. Servis, *J. Am. Chem. Soc.*, **89**, 1508 (1967)] and of 2-methoxy-3,5-dinitropyridine [C. Abbolito, C. Iavarone, G. Illuminati, F. Stegel and Vezzoler, *J. Am. Chem. Soc.*, **91**, 6746 (1969)].
- (8) K. L. Servis [*J. Am. Chem. Soc.*, **87**, 5495 (1965)] has given evidence for the transient formation from 2,4,6-trinitroanisole and methoxide of an adduct at  $C_3$ , which rapidly gives the stable classical Meisenheimer adduct at  $C_1$ .
- (9) R. A. Hoffman and S. Gronowitz, *Arkiv Kemi*, **16**, 563 (1960); R. F. M. White, *Phys. Methods in Heterocyclic Chem.*, **2**, 114-117 (1963).
- (10) M. J. Bulman, *Tetrahedron*, **25**, 1433 (1969).
- (11) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); *J. Am. Chem. Soc.*, **85**, 2870 (1963); (*note added in proof*) see also, A. A. Bothner-By, *Advan. Magn. Resonance*, **1**, 195 (1965); G. E. Maciel, J. W. Melver, N. S. Ostlund and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 4497, 4506 (1970); M. A. Cooper and S. L. Manatt, *ibid.*, **92**, 4646 (1970).
- (12) *E.g.*, an analogous low value of coupling constant for *ortho* hydrogen atoms in a similar system derived from benzene (Janovsky complex from 1,3-dinitrobenzene) has been measured by C. A. Fyfe and R. Foster [*Chem. Commun.*, 1219 (1967)], but the authors did not comment on this point.

Received August 12, 1970

90123 Palermo, Italy