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ARE THIOPHENES ATTACKED AT SULPHUR BY NITRENES?

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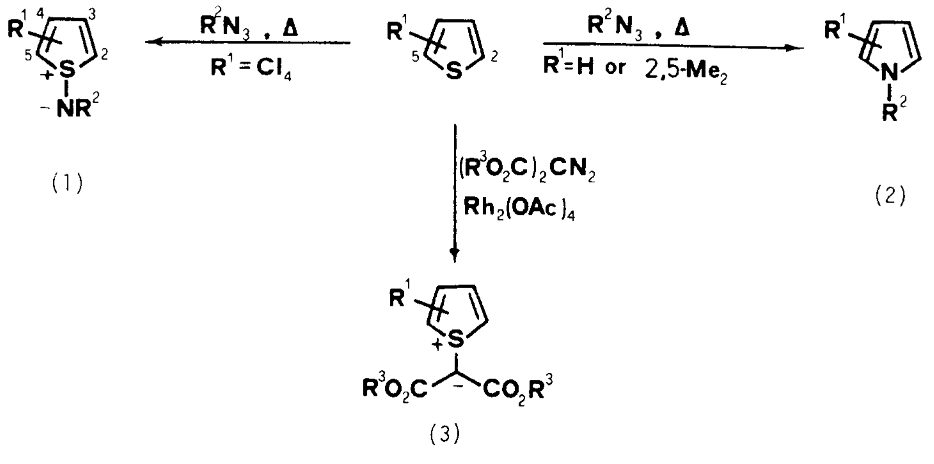
ABSTRACT: Ethyl azidoformate is shown to attack a range of thiophenes at sulphur giving transient S,N-ylides which can be trapped with acenaphthylene as [4+2] adducts; thiophene yields self-trapped products also.

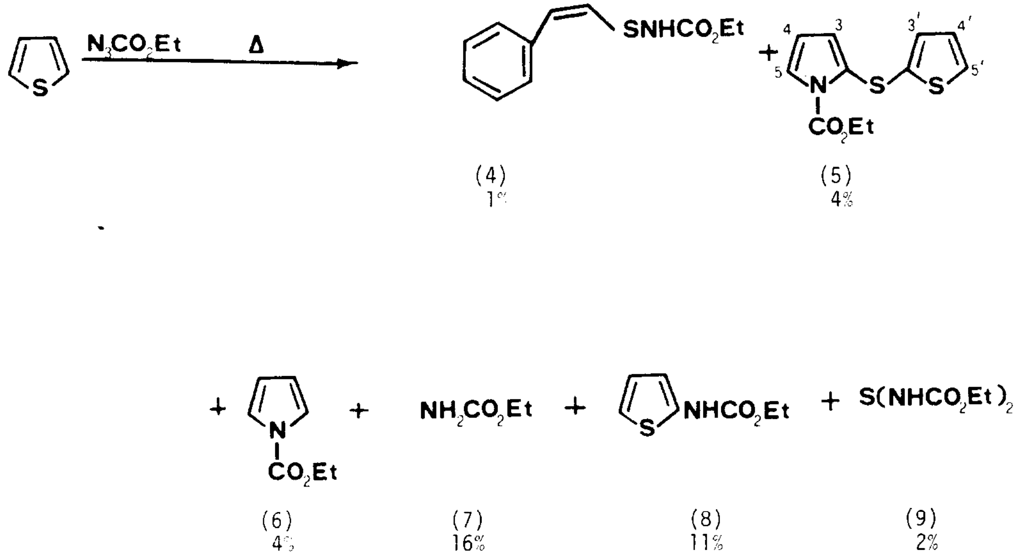
We recently observed that tetrachlorothiophene, apparently uniquely amongst thiophenes, yielded S,N-ylides (1) by the action of alkoxycarbonyl- or sulphonyl- nitrenes[1]. This is in contrast to the known reaction of ethoxycarbonylnitrene with thiophene or 2,5-dimethylthiophene which yields pyrroles (2) by attack at carbon[2] and the general reactivity of thiophenes with diazomalonates under rhodium catalysis to give S,C-ylides[3](3). (Scheme 1).



Scheme 1

That stable S,N-ylide formation is apparently unique is indicated by the fact that a wide range of thiophenes did not yield S,N-ylides, even when, for example one α-chlorine of tetrachlorothiophene was replaced by fluorine or the two β-chlorines were replaced by hydrogen, bromine or methyl groups. However, we wish to demonstrate in this letter that thiophenes in general do react at sulphur to give transient, trappable ylides (1), making the tetrachloro-derivative unique only as regards its stability[4].

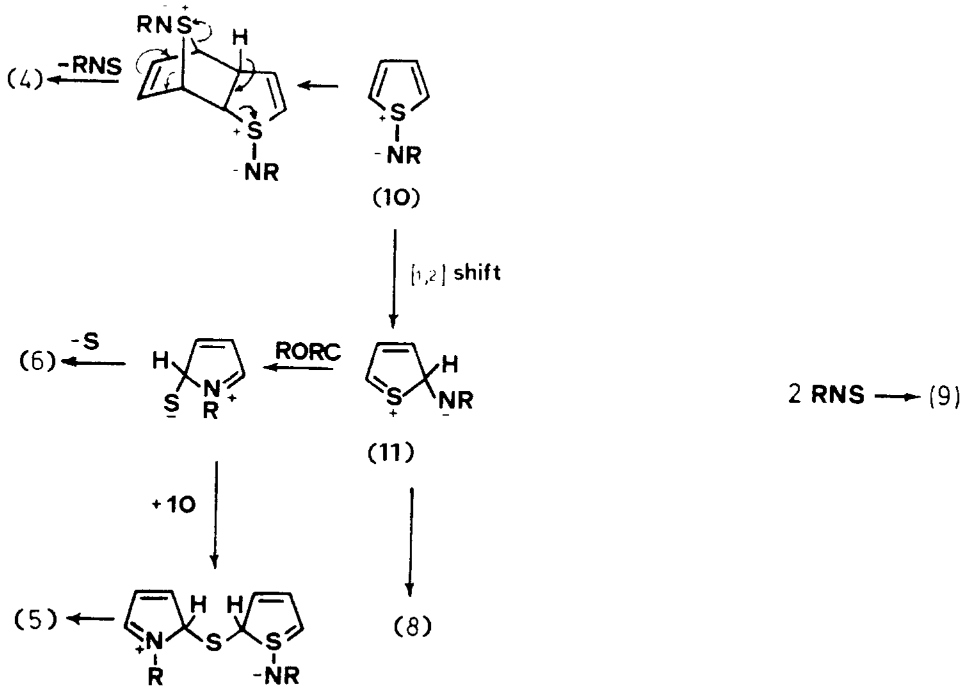
We first studied carefully the reported reaction of thiophene with ethyl azidoformate by thermolysing the latter (7.0g) in the former (80ml) at 130° for 1h in a teflon-lined autoclave. We isolated several fascinating products not reported by Hafner and Kaiser[2], indicative of ylide formation (Scheme 2). The earlier workers[2] reported isolating



Scheme 2

products (6,21%), (7,18%) and (9) and sulphur. The additional products (4&5)[5] as well as thiodiurethane (9) are best explained as derivatives of the thiophene S,N-ylide (10). (Scheme 3).

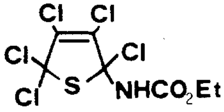
Indeed all the products are potentially derivable from the ylide. Thus the ylide could dimerise as is well documented for thiophene S-oxide and after elimination of the bridging RNS group (as is well established for the ylide cycloadditions[6]), the styrene (4) would arise. We have observed similar styrenes to derive from furan and dimethylbutadiene adducts of the tetrachlorothiophene ylides (1)[6]. 1,2-Shift of the ylide moiety would lead to a 2-carbamoylthiophene (11) readily transformable (i) by rearrangement and loss of sulphur into the pyrrole (6), (ii) by H-shift into the N-thienylcarbamate (8) and (iii) by further S-nucleophilic attack of the ylide (10) into the thienyl pyrrolyl sulphide (5). Tetrachlorothiophene ylide (1, $R^1=Cl_4$, $R^2=CO_2Et$) is thermally converted into the stable, vacuum distillable (180°) urethane (12) in confirmation of the proposed 1,2-shift. Finally the thiodiurethane (9) is known to arise from the thionitroso-compound[6], ejected in two of the above sequences. Clearly some of these products (e.g. 6-8) are also available in a non-ylide mediated pathway.



Scheme 3 (R = CO_2Et)

In order to further verify the role of the ylides (1) in nitrene attack of thiophenes, several thiophenes were thermolysed with ethyl azidoformate in methylene chloride solution with added acenapthylene (13), known to be a very effective dienophile for reaction with tetrachlorothiophene S,N-ylides[6]. In most cases a fluoranthene (14) or its 6b,10a-dihydro-derivative was isolated, indicative, as with the tetrachlorothiophene derivative (1), of ylide cycloaddition and bridge extrusion. Thus thiophene (3%), 2,5-dimethylthiophene (4.5%), 2,5-dichlorothiophene (10%), 2,5-dimethoxythiophene (3%), 2,5-dichloro-3,4-dibromothiophene (20%) and tetrabromothiophene (1%) all yielded fluoranthenes, the halo-substituted adducts being isolated as their 6b,10a-hydro derivatives.

We conclude that S-attack is a common phenomenon in thiophene-nitrene interactions. The question that should now be addressed is, do thiophenes tend to react with all hard electophiles at sulphur?



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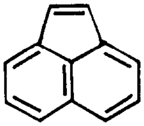

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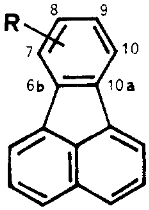

(14)

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1. O. Meth-Cohn and G. van Vuuren, J. Chem. Soc., Chem. Common., 1984, 190; J. Chem. Soc., Perkin Trans 1, in press.
2. K. Hafner and W. Kaiser, Tetrahedron Lett., 1964, 2185.
3. R.J. Gillespie, J. Murray-Rust, P. Murray-Rust, and A.E.A. Porter, J. Chem. Soc., Chem. Common., 1978, 83; R.J. Gillespie and A.E.A. Porter, J. Chem. Soc.,Perkin Trans. 1, 1979, 264.
4. The remarkable stabilising effect of perchloro-systems is well known as for example in the incredibly stable radicals of Ballester and co-workers, J. Org. Chem., 1982, 4, 259 and J. Chem. Soc., Chem. Common., 1983, 982.
5. Compound 4: ν_{max} (film) 3400(NH), 1730cm^{-1}(CO). δ_H($CDCl_3$) 1.29t(Me), 4.24q(CH_2) 5.89bs(NH), 6.30d and 6.40d (J=10Hz, CH=CH), 7.1-7.5m (aromatic H's). δ_C($CDCl_3$) 14.3q, 62.8t, 124.8d, 127.0d, 128.3d, 128.7d, 132.4d, 156.9s.
   Compound 5: ν_{max} (film) 1730cm^{-1}(CO). δ_H($CDCl_3$) 1.30t(Me), 4.36q(CH_2), 5.83dd(J=3.3 and 1.8Hz, H-3), 6.06t(J=3.5Hz, H-4), 6.95dd(J=5.4 and 3.6Hz, H-4'), 7.1-7.25m (-3' and 5), 7.32dd (J=5.4 and 1.8Hz, H-5'). δ_C($CDCl_3$) 13.9q, 63.5t, 111.6d, 114.9d, 121.9d, 127.4d, 130.4d, 131.7s, 134.6d, 136.4s, 149.9s. M.S. 253(M^+), 180($M-CO_2Et$), 136, 98, 71, 45.
6. O. Meth-Cohn and G. van Vuuren, J. Chem. Soc., Chem. Common., 1984, 1144; J. Chem. Soc. Perkin Trans. 1, in press.

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