The Action of Nitrenes on Halogenothiophenes; Formation of Thiophene S,N-Ylides

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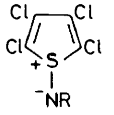
When ethyl or phenyl azidoformate, or *p*-tolylsulphonyl azide are decomposed in warm tetrachlorothiophene, tetrachlorothiophene S,N-ylides are formed; 2,5-dichloro-, 2,5-dibromo-, and tetrabromo-thiophene on the other hand give products arising from attack at the α-position followed by rearrangement.

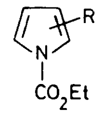
Sulphur–nitrogen ylides (sulphimides or sulphilimines) are well known and readily available.[1] However, despite a number of attempts,[2] the preparation of such ylides incorporating the sulphur atom of a thiophene has so far been unsuccessful. We herein report the first examples of such thienium *S*-imides (**1**).

Hafner and Kaiser[3] have shown that ethoxycarbonylnitrene readily attacks thiophene and its simple alkyl derivatives to give primarily pyrroles (**2**), a process which we interpret as an electrophilic attack at the α-position followed by ring-opening, ring-closure to a pyrrole, and sulphur elimination.[2] This pathway is also followed by some intramolecular analogues of this reaction.[2] Nitrenes tend to be halophobic and since polyhalogeno-substitution tends to stabilise reactive intermediates, we have examined the reaction of some nitrenes with halogenothiophenes.

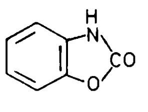
Ethyl azidoformate decomposed cleanly at 130 °C in tetrachlorothiophene solution (5% w/w; *ca.* 40 min) and when the solvent was removed *in vacuo,* a crystalline residue remained, readily purified by elution through silica (CH_2Cl_2) followed by recrystallisation from ethanol or light petroleum. The product (44%) shows no NH but a carbonyl absorption (1660 cm^{-1}) in its i.r. spectrum, gives analyses (C,H,N,S,) consistent with the formula $C_7H_5Cl_4SO_2$, shows an appropriate group of molecular ions and ions for tetrachlorothiophene as the base peak in its mass spectrum, and, most definitively, shows only two thiophenic carbon absorptions (δ 131.1 and 131.4 p.p.m., $CDCl_3$) in its ^{13}C n.m.r. spectrum as well as appropriate ethoxycarbonyl signals [δ 160.8 (CO), 62.5 (CH_2), and 13.7 p.p.m. (CH_3)].



(**1**)



(**2**)

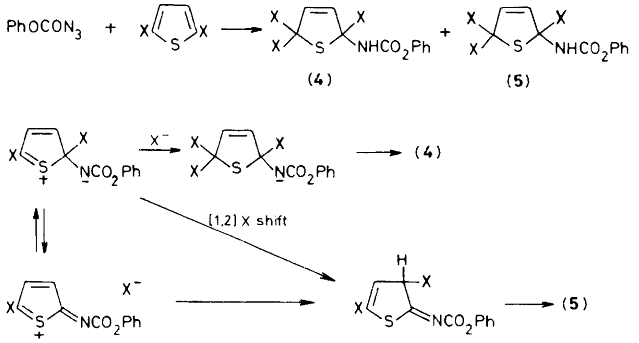


(**3**)

(**1a**); R = CO_2Et, m.p. 118—120 °C
(**1b**); R = CO_2Ph, m.p. 131—132 °C
(**1c**); R = $SO_2C_6H_4Me$-*p*, m.p. 173—174 °C

These data are consistent with structure (**1a**), which is further supported by the fact that on hydrogenolysis (Raney nickel and hydrogen) the compound readily gave tetrachlorothiophene and ethyl carbamate (68% yield). Furthermore, photolysis of the product in cyclohexane rapidly and cleanly yielded ethyl cyclohexylcarbamate (81%) and tetrachlorothiophene (85%) indicative of the reformation of ethoxycarbonylnitrene in a manner characteristic of sulphimides.[1]

In a similar manner phenyl azidoformate and *p*-tolylsulphonyl azide reacted with tetrachlorothiophene to give the ylides (**1b**) and (**1c**), respectively, though the higher reaction temperatures (145 and 150 °C) necessary to accomplish the decomposition before thermal decomposition ensued inevitably resulted in lower yields (23 and 24%† respectively). Attempts to generate the latter ylide (**1c**) by the classical



	X	(4)		(5)	
		M.p. (*t*/°C)	% Yield	M.p. (*t*/°C)	% Yield
a	Cl	134—137	13	69—70	10
b	Br	144—145	15	106—107	15

Scheme 1

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† Based on reacted azide; reaction terminated after 48% of the theoretical nitrogen evolution.

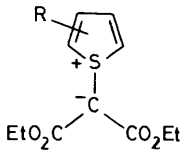
method[4] involving chloramine T and tetrachlorothiophene in 2-ethoxyethanol at 100 °C for 6 h, with or without added acetic acid, were ineffective, the reagents being unchanged. Photolysis of the phenoxycarbonyl ylide (**1b**) in methylene chloride solution gave benzoxazolone (**3**) (46%) again indicative of a nitrene intermediate.

2,5-Dichloro- and 2,5-dibromo-thiophene behaved quite differently giving in each case two products (**4**) and (**5**). The structure of (**5b**) was proved by its synthesis from 2,3,5-tribromothiophene [*via* the 2-lithio, 2-carboxylic acid, 2-carbonyl azide, and 2-isocyanate derivatives; phenol then gave the carbamate (**5b**)].

The compounds (**4**) showed NH (3260 cm^{-1}) and carbonyl i.r. absorptions (1720 cm^{-1}) and a *cis*-alkene in their ^{1}H n.m.r. spectra [(**4a**); δ 6.72 (d) and 7.02 (d, *J* 10.5 Hz); (**4b**): δ 6.7 (d) and 7.44 (d, *J* 10.5 Hz)]. Their mass spectra‡ are also in accord with the curious structures (**4**). On heating under reflux in tetrachloroethane for 4 h the trihalogenodihydrothiophenes (**4a**) and (**4b**) did not change. The formation of (**4**) and (**5**) is rationalised in Scheme 1.

When phenyl azidoformate is decomposed in refluxing tetrachloroethane solution, benzoxazolone (**3**) is formed in 65% yield. Similar action of phenyl azidoformate (5.0 g) on a solution of tetrabromothiophene (42.0 g) in tetrachloroethane (80 ml) gave benzoxazolone in even higher yield (82%) together with a small amount of phenyl *N*-(3,4,5-tribromothienyl)carbamate (1%).

The ylides (**1**) are the aza-analogues of the known carbon–sulphur ylides [*e.g.* (**6**)].[5]



(**6**)

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‡ (**4a**), *m/z* (^{35}Cl): 323 (M^+, 4%), 229 (M−PhOH, 22%), 194 (229−Cl, 15%), and 94 (PhOH, 100%); (**4b**), *m/z* (^{79}Br): 455 (M^+, 3%), 361 (M−PhOH, 3%), 282 (361−Br, 9%), 240 (282−NCO, 23%), 203 (282−Br, 12%), 161 (242−Br, 8%), and 94 (PhOH, 100%).

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